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PROOF OF CONCEPT FOR MANUFACTURING MICROFIBRILLATED CELLULOSE

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Fibre and Polymer Engineering

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Abstract of master's thesis

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Abstract

Some of the major challenges of our time drive the use of renewable and biodegradable products, like cellulose. When cellulose is disintegrated into its elemental constituents, microfibrils, unique properties arise. Microfibrillated cellulose, with its high surface area and huge bonding capacity, can enhance the strength of many products from paper to thermoplastics.

The purpose of this thesis is to prove that a continuous, commercial production of microfibrillated cellulose for papermaking applications by refining is feasible. Main experiments were carried out with ProLab™ laboratory refiner using bleached hardwood kraft pulp. Produced microfibrillated cellulose was characterized as itself and as a fraction in laboratory sheets. The literature review covers fundamentals of cellulose fibres, effects of processing on the fibres with focus on refining, and current and potential applications for microfibrillated cellulose with the focus on papermaking.

According to literature and backed up by the experiments, it can be concluded that a feasible production of MFC by refining alone is possible. Furthermore, it is the most reasonable mechanical production method in terms of cost and scalability. No chemical or enzymatic pre-treatment seems necessary. Produced MFC enhanced the strength of chemical and mechanical pulp. It was found that refining far beyond specific energy consumption of 500 kWh/t might not be practical, as refining efficiency and process configuration cause challenges beyond that point. At 500 kWh/t, the product is highly heterogeneous, but it should not be a problem in the target applications. It was also found that automated optical fibre analysers can provide enough information for a controlled, continuous production of MFC.

Keywords Microfibrillated cellulose, MFC, nanocellulose, refining, ProLab

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Abstract of master's thesis

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Työn nimi Mikrofibrilloidun selluloosan tuotantokonseptin toimivuuden osoitus

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Abstract

Monet aikamme suurimmista globaaleista haasteista ohjaavat uusiutuvien ja biohajoavien tuotteiden, kuten selluloosan, käyttöön. Selluloosasta saadaan esiin ainutlaatuisia ominaisuuksia hajotettaessa se pienimpiin rakenneosiinsa, mikrofibrilleihin. Näitä ominaisuuksia ovat muun muassa suuri ominaispinta-ala ja valtaisa kemiallinen sitoutumiskapasiteetti, jotka voivat lisätä lujuutta monissa tuotteissa paperista muoveihin.

Tämän työn tavoitteena on osoittaa mikrofibrilloidun selluloosan jatkuvatoimisen tuotantomenetelmän toimivuus paperiteollisuuden parissa. Kokeellinen osuus suoritettiin pääasiallisesti ProLab^{TM}-laboratoriojauhimella käyttäen valkaistua kemiallista koivumassaa. Tuotetun mikrofibrilloidun selluloosan luonnehdintaan käytettiin optisia ja fysikaalisia karakterisointimenetelmiä sekä mekaanisia kokeita laboratorioarkeille. Kirjallinen osuus kattaa selluloosan perusteet mikro- ja nanomittakaavassa, jauhatuksen ja muun prosessoinnin vaikutukset selluloosaan sekä nykyiset ja potentiaaliset sovellukset mikrofibrilloidulle selluloosalle erityisesti paperiteollisuudessa.

Kirjallisuuden ja kokeellisen osuuden perusteella jauhatus osoittautui kannattavaksi ja käytännölliseksi tavaksi tuottaa mikrofibrilloitua selluloosaa. Lisäksi jauhatus vaikuttaa selvästi käytännöllisimmältä mekaaniselta tuotantomenetelmältä teollisessa mittakaavassa. Tuotettu mikrofibrilloitu selluloosa lisäsi sekä kemiallisen että mekaanisen massan lujuutta. Kokeellinen osuus antoi vahvoja viitteitä siihen, ettei jauhatusta kannata jatkaa kovin paljoa yli 500 kWh/t spesifisen energiankulutuksen, vaikka tuote tässä vaiheessa onkin hyvin heterogeenistä. Jauhatus yli tämän arvon alentaa huomattavasti energiatehokkuutta sekä monimutkaistaa tarvittavaa tuotantolaitteistoa. Lisäksi havaittiin, että automaattiset optiset kuituanalysaattorit ovat tarpeeksi hyviä luonnehtimaan mikrofibrilloitua selluloosaa kontrolloidun, jatkuvatoimisen tuotannon mahdollistamiseksi.

Avainsanat Mikrofibrilloitu selluloosa, MFC, nanoselluloosa, jauhatus, ProLab

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This work was done in close cooperation with Erik Sjöström from Åbo Akademi. The chapters *Theories on refining* and *ProLab™* are summarized from Sjöström's work. Likewise, parts of this work were lent to Sjöström to be utilized in his work. I would like to thank Erik for his mechanic's skills and overall excellent cooperation.

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Vantaa 21.6.2018

Veikko Sajaniemi

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Noting

SEC 700 kWh/t = Net specific energy consumption of 700 kWh per ton

Abbreviations and symbols

α	Average intersecting angle (°)
AFM	Atomic Force Microscopy
BC	Bacterial Cellulose
BD	Bone Dry
C	Concentration (of pulp in water) (g/l)
CAS	Chemical Abstracts Service
CEL	Cutting Edge Length (m/rev)
CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofibrils
CS	Cationic Starch
CSF	Canadian Standard Freeness
CTMP	Chemi-thermomechanical pulp
IL	Refiner bar width factor (m)
IN	Amount of refining impacts (km/kg)
$\bar{l}$	Average length of bars (m or m/rev)
LC	Low Consistency (refining)
LPB	Liquid Packaging Board
L_s	Cutting speed of the bars (km/s)
M	Fibre flow (kg/s)
MFC	Microfibrillated Cellulose
n	Rotation speed (rev/s)
P	Power consumption (kWh)
rpm	Revolutions Per Minute
SEC	(Net) Specific Energy Consumption (kWh/t)
SEL	Specific Edge Load (J/m)
SEM	Scanning Electron Microscopy
SPCI	Swedish pulp and paper engineers' association
SR	Schopper-Riegler
SRE	Specific Refining Energy (kJ/kg)
SSA	Specific Surface Area (m^{-1})
SSL	Specific Surface Load (J/m^2)
TEM	Transmission Electron Microscopy
TMP	Thermomechanical pulp
TSI	Tensile Strength Index
$\dot{V}$	Flow (l/h)
w	Bar width (m)
WRV	Water Retention Value
z	Bar amount

1. Introduction

Cellulose is available in numerous sources including wood, annual plants, bacteria, and sea life. Though annual plants can have local significance, wood is the foremost source of cellulose. Some of the major challenges of our time - climate change, population growth, and environmental pollution - drive the use of renewable and biodegradable solutions. Wood binds carbon as it grows and products made of it act as carbon sinks for the duration of their lifespan. At the end of it, wood-based products can be used as carbon neutral source of energy, or recycled into new products.

Extraction of cellulose from wood has many advantages. Wood is widely available in almost every habitable corner of the world and the technology and infrastructure to tap into this raw material is well developed. Unlike many other bioproducts like corn-based bioethanol and starch, wood does not directly compete with food production.

When cellulose is disintegrated into its elemental constituents, microfibrils, unique properties arise. Microfibrillated cellulose, with its high surface area and huge bonding capacity, can enhance the strength of many products from paper to thermoplastics. The search for novel fibre based products has sparked an exponential increase in publications and patents considering micro- and nanocelluloses (Figure 1).

The purpose of this thesis is to proof that microfibrillated cellulose can be feasibly produced by refining. Needs of a continuous, commercial production for papermaking applications integrated to a mill are considered. Furthermore, the aim is to proof that manufacturing can be carried out with specialized refiner fillings without any chemical or enzymatic pre-treatments. Refining is assumed to be the most feasible mechanical production method in commercial scale, which is evaluated in the literature review. Total energy consumption and the price of energy are considered. An experimental comparison to cationic starch is made. Main experiments are carried out with ProLab^{TM} laboratory refiner using bleached hardwood kraft pulp. Produced microfibrillated cellulose is characterized as itself and as a fraction in laboratory sheets. Significance of hornification

considering manufacture, end-product, and applications, is studied. The aim of the literature review is to cover fundamentals of cellulose fibres, effects of processing on the fibres with focus on refining, and current and potential applications for microfibrillated cellulose with the focus on papermaking.

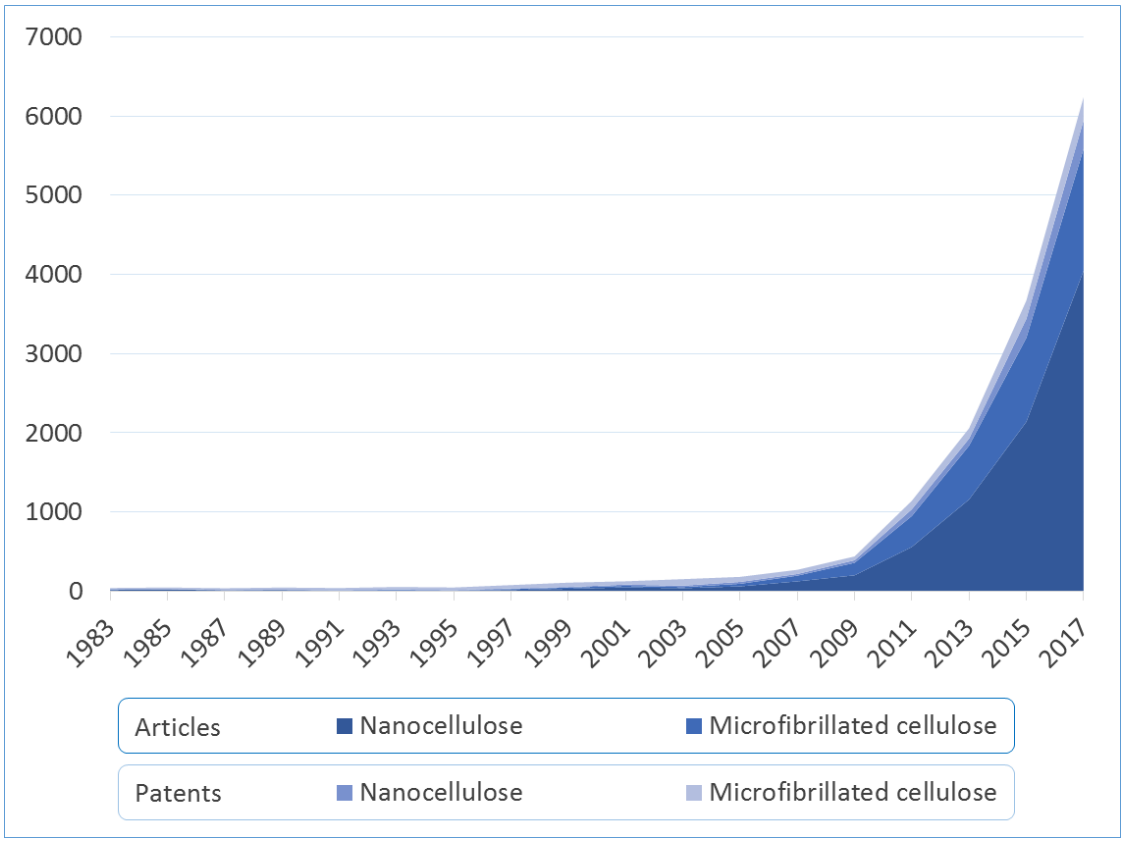

Figure 1. Number of publications found by Google Scholar with selected search terms.

2. Cellulose

Cellulose is widely used in construction, packaging and as a conveyor of information. Applications of higher value in fields like pharmaceuticals and food industry have been, and are being, developed. New horizons turn up in the advancement of existing products as well. An example of these is the use of microfibrillated cellulose as a strength enhancement agent in paper and board (Kangas 2014).

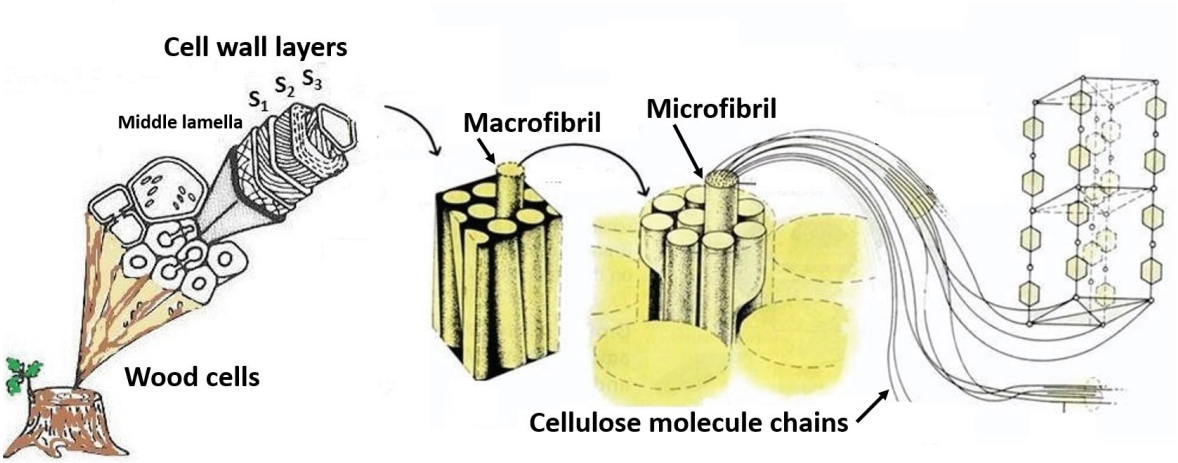

Figure 2. Schematic structure of cellulose in wood, modified from Dimic-Misic (2014).

In nature, cellulose exists as hierarchically structured fibres consisting of β-D-glucose molecules. These molecules form microfibrils through a network of inter and intramolecular hydrogen bonds. In wood, microfibrils aggregate into roughly rectangular shaped bundles with other natural polymers, lignin and hemicelluloses, in between the bundles. The microfibril bundles form a layered structure, the fibre, with hollow lumen in the centre and amorphous regions called middle lamellae, rich in lignin and hemicelluloses, between individual fibres (Janardhnan, Sain 2007, Fahlén 2005, Sundholm 2007). Typically, softwood and hardwood contain 20-30 % and 25-35 % of hemicelluloses and 25-30 % and 20-25 % of lignin, respectively. Both wood types contain some 40-45 % cellulose. Other compounds, mainly extractives, make up some 5 % of the wood dry solids (Sundholm 2007, Willför, Alén et al. 2011).

Cellulose is chemically very stable and can only be degraded by strong acids or chemical systems with strong hydrogen bond breaking ability. Cellulose is dimensionally stable in a

wide range of temperatures, though not in varying moisture content as water makes the fibres swell. Glass transition of cellulose is estimated to take place at around 180-200 °C and thermal degradation occurs well above 300 °C. Cellulose surface, having three reactive hydrogen groups within each glucose molecule, can be modified with relative ease. Cellulose molecules are naturally self-adhesive, both at nanoscale and at microscale (Gardner, Oporto et al. 2008, Abe, Yano 2009, Chow, Pickles 2007).

2.1 Fibre structure and physical phenomena

Cellulose fibre is a layered, hollow tube with amorphous middle lamella rich in hemicelluloses and lignin in between individual fibres (Figure 3). The lumen in the middle transports water from the roots to the crown. Cellulose cell wall consists of several layers, oriented at characteristic angles. S2 layer takes up the bulk of the cell wall and gives fibre most of its strength. S2 layer has an angle between 0° and 30°, depending on which part of the tree the fibre is located. P and S1 layers are often lost in pulping process (Kainulainen, Kajanto et al. 1998, Fahlén 2005).

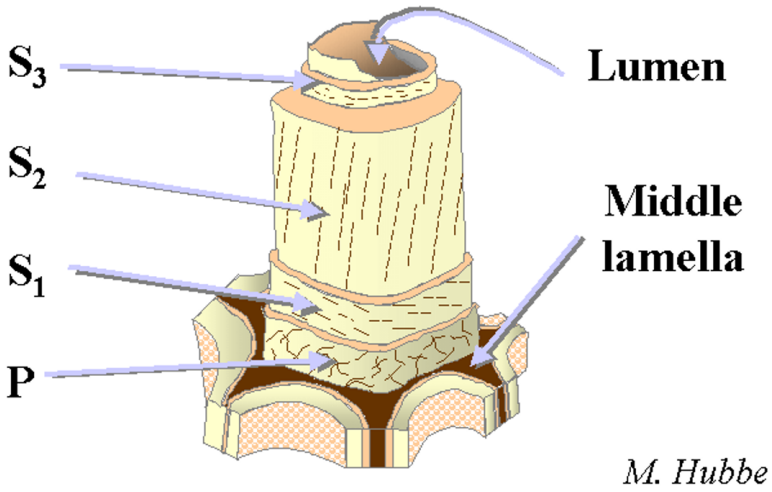

Figure 3. Fibre wall sublayers (Hubbe 2018).

Cellulose fibres are plant cells with high aspect ratio, typically between 50 and 100. Depending on the species, wood can contain a significant portion of non-fibre cells. For example, in beech the fibres comprise only 40 % of the total volume, whereas softwood species constitute primarily of fibre cells called tracheids. Other cell types, like

parenchyma cells, ray cells and vessel elements, are often detrimental to papermaking processes and paper properties (Fahlén 2005, Kainulainen et al. 1998, Plomion, Leprovost et al. 2001).

In this chapter, the fibre ultrastructure, bonding mechanisms and hornification are discussed.

2.1.1 Fibre ultrastructure

Cellulose fibres are up to several millimetres long and some tens of microns wide. Fibres constitute of microfibrils, small bundles of mostly cellulose molecules (Fahlén 2005, Kainulainen et al. 1998). Fahlén (2005) examined the ultrastructure, the intermediate nanoscale, of spruce tracheids in kraft pulp with atomic force microscopy (AFM) (Figure 4). Fahlén (2005) found that the S2 layer in the fibre wall has a concentric structure, meaning that the layered structure of fibres extends to the fibre ultrastructure. In a spruce tracheid the microfibrils, building blocks of fibres, are 4 nm in width forming microfibril aggregates averaging 15-16 nm in side length (Figure 5). Aggregates vary between 5-25 nm in width but the same average width can be found in any layer from P to S3. Between the microfibril aggregates are regions of more amorphous material with higher lignin and hemicellulose content than inside the aggregates. Thus, the structure of wood repeats itself in micro and nanoscale. In conventional refining, the energy is not high enough to disintegrate the microfibril aggregates, but rather separate them into external fibrillation and fines. This is backed up by the findings of Laine et al. (2004), who also suggested the same microfibril aggregate structure with regions of hemicelluloses, lignin and water filled pores in between. As these dimensions correspond to the observed dimensions of MFC (Ankerfors 2015), same should hold true for the far more intensive processing methods like microfluidization and homogenization. Thus, it can be concluded that MFC constitutes of the elemental microfibril aggregates and, depending on the degree of fibrillation, bundles of them.

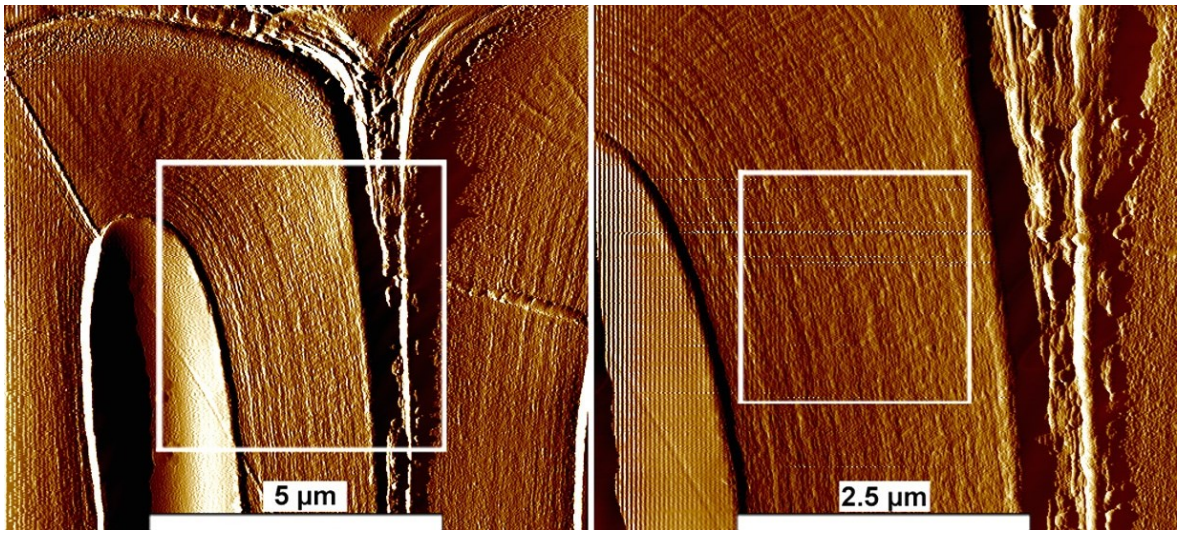

Figure 4. AFM phase images of wood fibres in the transverse direction (Fahlén, 2005).

However durable the microfibril aggregates may be, Fahlén (2005) observed approximately 1 nm shrinkage in them upon drying. Fahlén (2005) concludes that some water is bound to hemicelluloses and disordered cellulose inside the aggregates, though most of the shrinkage appeared in the amorphous region between the aggregates. This is logical, since this region is rich in lignin. Lignin is mostly dissolved in kraft pulping leaving pores in the structure that can collapse upon drying. Indeed, the decrease in pore volume was observed along with hornification. Likely the collapsing pores can also bring microfibril aggregates in close contact and form bonds unaffected by microfibrillation leading to larger microfibrils than would be gained from neverdried pulp.

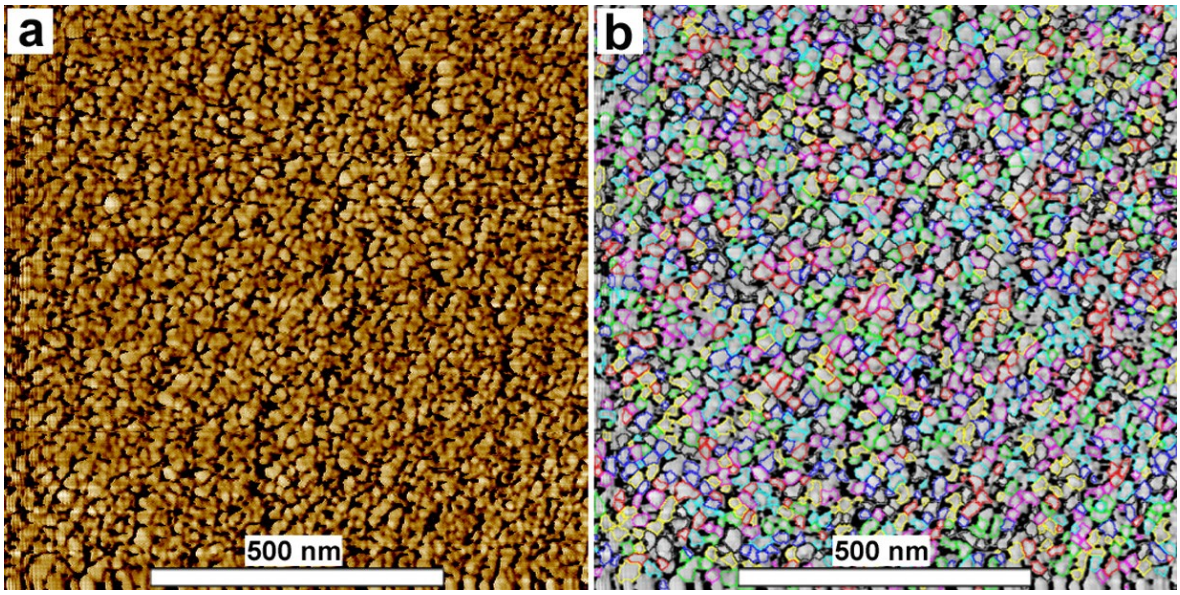

Figure 5. AFM images of wood fibre cross-section with microfibril aggregates clearly visible (Fahlén, 2005).

Furthermore, Fahlén (2005) observed a 25 % increase in the average microfibril aggregate size during kraft process. The chemicals or refining alone did not produce such effect. Hence it was concluded, that the high temperature in water saturation state in kraft cooking softens the amorphous parts of fibres enabling smaller and more mobile aggregates to attach to adjacent ones.

2.1.2 Fibre bonding

In a pulp suspension, several types of bonds are present. Chemical bonds and acid-base interactions hold molecules together, van der Waals forces take effect on intermolecular level and physical entanglement occurs between polymer chains. Forming of paper and the interconnected fibre network therein utilizes all three bonding types. Mechanical properties of paper are mainly attributed to hydrogen bonds, i.e. bonds between covalently bonded hydroxyl group and an electronegative atom or molecule, usually oxygen. Structure of this type of a bond can be described as follows: H-O··H, "-" being covalent and "··" a hydrogen bond. Hydrogen bonds that form the crystal structure of cellulose are in principle the same as the ones in inter-fibre bonds or bonds between hydroxyl groups and water (Kainulainen et al. 1998).

For any bonding to happen, two fibres need to come in close proximity with each other. External fibrillation of fibres produces fibrils that can interlock mechanically pulling fibres closer together. This phenomenon is called the Campbell effect and it is highly dependent on the specific surface area (SSA), which is discussed more thoroughly in the section *4.2.2 Fines*. However, mechanical entanglement is a very complex occurrence and the strength of this type of bonding varies profoundly. Accordingly, the cohesion of wet web is attributed to van der Waals forces. Van der Waals forces are weak in relation to other type of bonding (Table 1), but they interact at much larger distances than chemical bonds. With progressing water removal, more hydrogen bonds between fibres take place giving paper its characteristic strength properties. In finished paper there are virtually no free, unbonded hydroxyl groups left. In polar liquids like water, surface tension has a major role bringing fibre surfaces together upon water removal. This effect is discussed in detail in the next section, *2.1.3 Hornification* (Kainulainen et al. 1998).

Table 1. Strength of most essential chemical bonds in fibre networks (Brown et al. 2017, Kainulainen et al. 1998).

	Covalent O-H -bond	Hydrogen bond O··H	van der Waals
Indicative bond length	0.1 nm	0.17 nm	0.3-0.5 nm
Bond strength	460 kJ/mol	8-32 kJ/mol	2-8 kJ/mol

2.1.3 Hornification

Hornification is a technical term used to describe the partly irreversible changes in fibre structure upon drying. These changes result from hydrogen and van der Waals bonding formed by collapse of macropores and bonding of external fibrillation and fines with each other or to the fibre surface. Wet pressing and calendering are known to cause similar pore collapse as water removal. Macropores are mainly left by dissolved lignin and hemicelluloses in pulp cooking. Thus, hornification is more evident in chemical than mechanical pulps. Micropores, pores less than 1 micron in diameter, are less or non-affected by hornification, as the water in these is bound by increasing surface tension as the pore size gets smaller (Kainulainen et al. 1998, Fahlén 2005, Hubbe, Venditti et al. 2007, Maloney, Li et al. 1997, Maloney, Paulapuro 1999).

Hornification induces a loss in water holding capacity, a loss in conformability i.e. stiffening, reduces the surface area and causes fibre shrinkage. (Hubbe et al. 2007, Letková, Letko et al. 2011, Spence, Venditti et al. 2010, Diniz, Gil et al. 2004, Minor 1994). Loss in water holding capacity has been demonstrated by measuring the water retention value (WRV) of fibres prior to and after drying. Letková et al. (2011) reported a 10 % decrease in WRV after one drying cycle with bleached hardwood kraft pulp. Reduced WRV, the amount of water contained in pulp after centrifuge filtration (Kainulainen et al. 1998), means less swelling and less energy needed in water removal at a paper machine. In certain paper grades, e.g. printing, file folder and boxboard, more bulky structure caused by the stiffened fibres is an advantage. Also, less swelling means more dimensional stability, which can be an advantage (Hubbe et al. 2007). According to Diniz et al. (2004), decrease in WRV correlates well with the amount of drying cycles. Thorough measurements on WRV were carried out by Yamauchi and Amano (2014), who imposed 30 drying and wetting cycles on dissolved and kraft pulp. Drop in WRV was most

prominent in the first three cycles totalling up to a 50 % decrease, but started to level off afterwards ending at a level of around 60 %. No fundamental difference in drying and rewetting behaviour between dissolved and kraft pulp was observed.

In papermaking, refining is used to activate the fibres by several ways enhancing bonding and other qualities. More intensive refining and higher wet pressing pressure promote more severe hornification. Likewise, the more lignin and hemicelluloses are dissolved in chemical pulping, more severe hornification occurs. Hornification causes deactivation of the fibre surface leading to a decreased inter-fibre bonding, thus reducing strength. However, wet end additives and blending with well refined, neverdried pulp can alleviate the deactivation (Hubbe et al. 2007, Letková et al. 2011, Maloney, Paulapuro 1999, Howard 1990).

The effects of hornification can be reversed to some degree by refining (Maloney, Paulapuro 1999, Kitayama, Okayama et al. 1987, C. Laine et al. 2004), by bulking agents like adsorbed sucrose (Minor 1994), and by spacer group insertion or alkali cooking (Diniz et al. 2004), but the collapse of macropores is deemed irreversible and normal refining energy is not enough to break these bonds. Instead, refining opens new macropores at weaker points in the fibre. Lost external fibrillation can be reproduced by refining. However, reverse of hornification has its downsides, as refining reduces fibre length and consumes energy.

Several papers have been published on prevention of hornification. Song and Law (2010) found that mild TEMPO oxidation of fibres prior to drying can prevent decrease in WRV. Similar results have been reported by others as summarized in the work of Minor (1994). It is logical that increased surface charge density i.e. increased repulsion between cellulose fibres should reduce the formation of irreversible bonding. Also, residual lignin has been associated with reduced hornification (Spence et al. 2010). However, as Song and Law (2010) stated, surface treatment can lead to decrease in various strength properties and bulk. Further oxidation also reduced WRV indicating less available hydrogen bonds for water, or fibres, to attach to. Yasnovsky and MacDonald (1983)

patented a method using high pressure and temperature in alkaline conditions that is claimed to prevent hornification.

Though the effects of hornification are rather well agreed in the scientific community, exact mechanisms in the micro- and nanolevel are difficult to characterize and cause some dispute. Diniz et al. (2004) argue that hornification is a "particular case of lactone bridge formation in lignocellulosic materials", supporting their claim by several papers published in the 1950's and 1960's. It has been demonstrated that carboxylic acid groups can undergo an esterification reaction with hydroxyl and that lactone is present in dried pulp, but not in the neverdried. Also, a connection between hornification and lactone bridge destroying treatment has been found. Diniz et al. (2004) acknowledge the role of hydrogen bonds, but state that the covalent lactone bridges dominate the swelling behaviour. The team concludes it unreasonable for water removal to cause hydrogen bonding that is partially reversible and partially not. However, hornification is a confirmed phenomenon also in bacterial cellulose (Liebner, Haimer et al. 2010) and dissolved pulp (Yamauchi, Amano 2014), that have very little or no residual hemicellulose or lignin that can produce carboxylic groups on cellulose fibres. Also, as it is mainly the strong hydrogen bonding that keep cellulose crystals together (Fahlén 2005), it is quite clear that some hydrogen bonds within the fibre are more susceptible to breakage by water than others. Lactone bridging can have an impact on hornification, but it is hardly the whole truth as majority of the scientific community endorses the theory of irreversible hydrogen bonding.

2.1.4 Hornification in MFC

The changes in fibre structure caused by hornification have effects on fibre processing, water interactions and end-product properties. Spence et al. (2010) studied the differences of MFC films made of various pulps, some of them dried and some neverdried. MFC was produced by homogenization after a refining pre-treatment. The films made of once-dried pulp had properties comparable to those of neverdried origin in terms of density, roughness, fold endurance and tensile properties. Based on these findings, hornification does not have significant effect on MFC in film making. However,

the study did not consider water interactions or effects on processability. It should be noted, that direct conclusions to papermaking cannot be drawn from cast films.

Yong (2017) produced CNF with a grinder and concluded that hornification caused inferior fibrillation characteristics for recycled pulp compared to kraft pulp. They also found that degree of crystallinity increases in recycling as amorphous regions are disintegrated. If disintegration of amorphous cellulose is evident in normal recycled fibre processing, the effect might be considerable in MFC production with much more intensive mechanical stress. However, no literature reference of this was found. It could be, that recycling processes and various fibrillation methods are fundamentally too different from each other for this particular phenomenon to happen in both.

Utilizing the quality index the team created for MFC benchmarking, Desmaisons et al. (2017) found that MFC from dried pulp was 15 % worse than MFC from neverdried pulp. The quality index combines eight optical, mechanical, and other physical characterization methods. Similar results were published by Kekäläinen et al. (2014). The team found that hornification caused difficulties in the disintegration of fibres into MFC. More fibre cutting occurred compared to neverdried pulp. Kekäläinen et al. (2014) concluded that MFC production from hornified pulp demands more energy, and more chemicals if such are used, than neverdried pulp.

Kainulainen et al. (1998) named higher stiffness, curliness, brittleness and shorter fibre length as the properties of recycled pulp in comparison to virgin, neverdried fibre. Shorter fibre length might be an advantage in highly fibrillated products reducing refiner clogging (Andresen, Johansson et al. 2006). The downside with stiffer fibres is the reduced conformability for bonding, thus requiring higher refining energy compared to neverdried fibres when a specific bonding capacity is targeted. Also, in the case of recycled fibres, any pigments, sand and other residuals can damage the refiner fillings and decrease their lifespan, especially with the very narrow rotor blades as required for microfibrillated products (Bilodeau, Paradis 2015).

3. Micro- and nanocelluloses

By disintegrating the fibres into their elemental components, microfibrils, materials with extraordinary properties are attained (Figure 6). These materials, called micro- and nanocelluloses, are strong, elastic, highly hydrophilic, and relatively easy to modify chemically. They have high surface area, bonding capacity, and aspect ratio, and produce strong, shear thinning gels even at low consistencies (Kangas 2014, Eichhorn, Dufresne et al. 2010, Nakagaito, Yano 2005). Terms microcellulose and nanocellulose are used crosswise in the literature and refer to materials with at least one dimension between 1-100 nm (Kangas 2014, Chinga-Carrasco 2013, Nakagaito, Yano 2005). Microcellulose can be used to describe a more heterogeneous material with some of its particles in nanoscale and some in microscale. Likewise, nanocellulose is a more homogeneous product with all or almost all of its particles in the nanoscale (Chinga-Carrasco 2013, Taipale, Österberg et al. 2010). The negative connotations of word "nano" in consumer business can promote the use of term microcellulose. Generally, nanoscale cellulose is divided into micro- or nanofibrillated cellulose (MFC/NFC), cellulose nanocrystals (CNC) and bacterial cellulose (BC), synthesized by *Acetobacter xylinum* bacterium (Kangas 2014) (Figure 7). In this chapter, these three archetypes of nanocellulose are discussed in detail with the focus on microfibrillated cellulose.

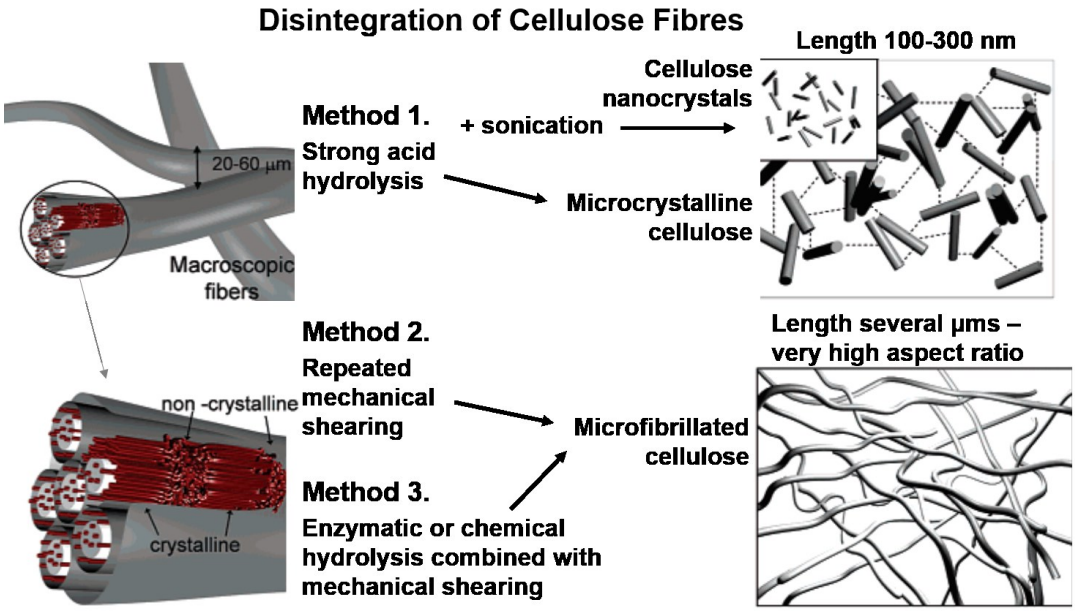

Figure 6. Plant-based micro- and nanocelluloses, adapted from (Pääkkö, Ankerfors et al. 2007)).

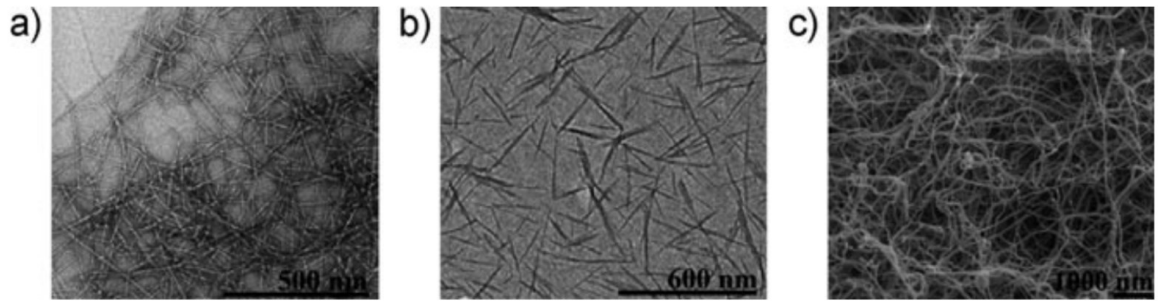

Figure 7. TEM images of a) MFC and b) CNC; SEM image of c) BNC (Klemm, Kramer et al. 2011).

3.1 Microfibrillated cellulose

In the early 1980's, Turbak et al. (1981) and Herrick (1983), found that high shear homogenization of cellulose produced thick, highly viscous and stable suspension. Turbak et al. established the term microfibrillated cellulose (MFC). MFC is characterized as a semi-crystalline product with diameter of 5-40 nm and length several micrometres. MFC is highly branched, flexible and has very high aspect ratio. It forms a densely interconnected network (Figure 8) and has a strong tendency to aggregate, especially upon drying (Ankerfors 2015, Kangas 2014).

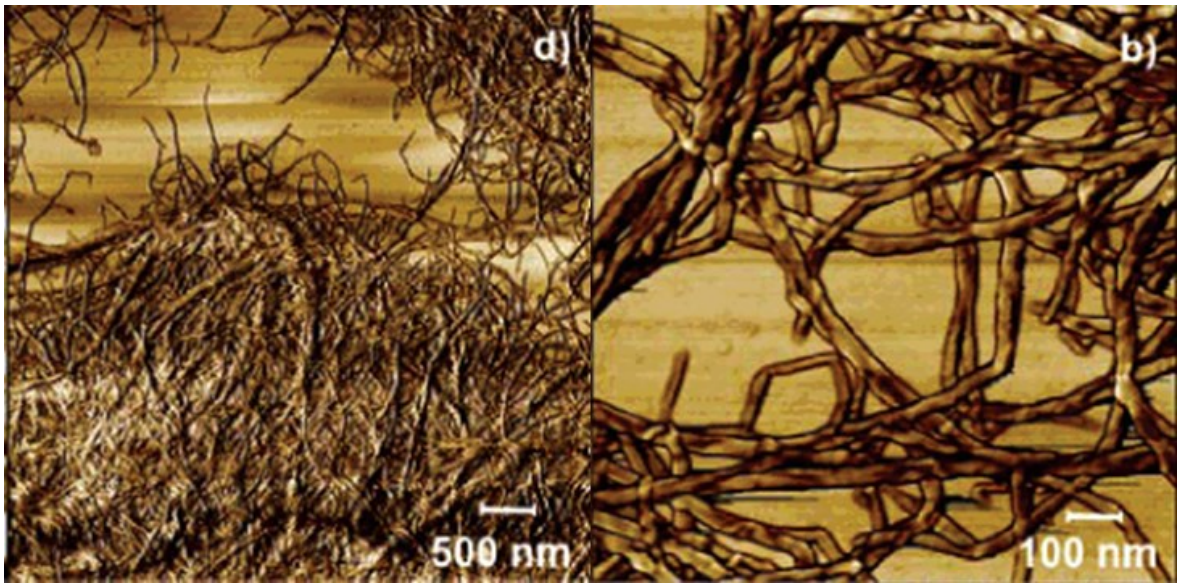

Figure 8. Phase-contrast AFM images of dried MFC (Pääkkö et al. 2007).

High shear mechanical treatment of cellulose fibrillates the fibre cell wall separating microfibrils from each other. The degree of fibrillation with mechanical disintegration is

non-uniform yielding heterogeneous material. Besides nano- and microscale fibrils, some wholly intact fibres can be present in the end-product. Chemical or enzymatic pre-treatments can yield more homogeneous MFC (Kangas 2014). In addition to homogenization, refining, microfluidization, cryocrushing, and ball milling can be used in MFC production (Turbak et al. 1981, Spence, Venditti et al. 2011, Zhang, Tsuzuki et al. 2015). Production methods and pre-treatments are described in detail in the chapter *4. Production of microfibrillated cellulose*.

First applications of MFC were in the food industry as thickeners or emulsion stabilizers, and since the 1980's the use of MFC has expanded to papermaking additives, coatings, barriers, cosmetics, pharmaceuticals, electronics, paintings, and several other fields (Ankerfors 2015, Kangas 2014). MFC applications can be divided into rheology modifiers, e.g. in concrete, emulsion stabilizers in e.g. the food industry and strength enhancers in papermaking and composites. The applications are discussed more thoroughly in the chapter *5. Applications of microfibrillated cellulose*.

Increasing resistance to water removal is one of the fundamental aspects of cellulose fibrillation. Thus, dewatering tests can be used to characterize MFC. Schopper-Riegler (SR) and Canadian standard freeness (CSF) are the two most common dewatering tests (Kainulainen et al. 1998). However, their results do not tell the exact degree of fibrillation and should always be used in comparison with other samples. Other widely used indicators for the degree of fibrillation are WRV and fibre saturation point (FSP), the total volume of water in pulp (Maloney, Paulapuro 1999), though they measure the water holding capacity instead of resistance to its removal.

Kangas (2014) compiled a thorough summary of micro- and nanocellulose characterization methods. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) are often used in laboratories to determine particle size, size distribution, branching, aspect ratio, amount and quality of dissolved and colloidal particles, fibril overall appearance, and even some mechanical properties. Nanomaterial can be fractionized by a centrifuge or by sieving. Viscosity and

gel strength can be determined by various rheology measurements. Mechanical properties are best evaluated by using standard mechanical tests with cast films or papers with moderate share of MFC. Various optical measurements tell about the particle size and size distribution - the more transparent a gel or a film is, the smaller the particles. Gel permeation chromatography (GPC) and size exclusion chromatography (SEC) are also used in MFC characterization. Furthermore, X-ray diffraction, X-ray scattering, conductometric titration, polyelectrolyte titration, and zeta-potential can be used to determine the crystallinity, specific surface area, surface charge, and surface chemistry of the product.

Desmaisons et al. (2017) have made an attempt at creating a quality index for benchmarking the various nano- and microfibrillated products. The quality index combines eight different measurements that do not require high level of expertise nor extremely expensive equipment. Such a quality index would be advantageous for both the industry and the academia enabling objective pricing and accurate comparison of research. However, the quality index needs further development and marketing for it to become widely accepted and utilized.

3.2 Cellulose nanocrystals

Cellulose nanocrystals (CNC) are manufactured by hydrolysing the disordered regions of cellulose with strong acid, typically sulphuric acid. Hydrolysed cellulose is then disintegrated with mechanical treatment or sonication. This way, highly crystalline rod-like particles are produced. CNCs are typically 2-20 nm wide and up to one micron long. The acid hydrolysis reduces fibril length leading to somewhat lower aspect ratio than that of MFC, typically between 10 and 100. CNCs are very stiff and the crystallinity of CNCs is up to 90 % (Aulin, Ahola et al. 2009, Kangas 2014). Sulphuric acid introduces sulphate ester groups with negative charge to CNC surface which enhances their dispersion in an aqueous media. Having high quantity of free hydrogen-groups on the surface, CNCs like other cellulose products, can be modified to meet the requirements of given application. In literature, terms like whiskers, rods, nanocrystalline cellulose, and their variations are used crosswise with cellulose nanocrystals (Kangas 2014).

For their high stiffness, CNCs have great potential as a reinforcement in nanocomposites. CNCs' tendency to organize in liquid makes it possible to use them in displays, specialty papers and functional packaging (Kangas 2014, Eichhorn et al. 2010). However, commercial use of CNCs is restricted by the expensive manufacture due to the low yield of 10-50 %, difficult purification and challenging recycling of sulphuric acid. Upon drying, CNCs form strong hydrogen bonds with each other forming microcrystalline cellulose (MCC). MCC can also be produced by strong acid hydrolysis leaving the mechanical disintegration out. MCC is stable and physiologically inert material that is in commercial use as a rheology modifier and binder in food and pharmaceutical industries (Kangas 2014).

A commercial partnership aiming at large scale MCC production has been announced by Aalto University in cooperation with process technology provider Andritz (Aalto University 2018). MCC production by AaltoCell™ technology is claimed to enable significant cost reductions compared to existing pilot plants. One disclosed application for the novel MCC would be its use as animal fodder.

3.3 Bacterial cellulose

Bacterial cellulose (BC) or bacterial nanocellulose (BNC) is cellulose synthesized by a small group of bacteria, mainly *Acetobacter xylinum*. By its physical properties and appearance, BC is virtually identical to MFC and could be classified as such. The main difference is in the manufacture process. MFC is produced top-down, disintegrating fibres, whereas BC is produced bottom-up (Figure 9). The bacteria synthesize cellulose into nanoscale ribbons by the polymerization of glucose molecules. Cellulose is then secreted through the cell wall yielding a highly viscous gel suspension. BC microfibrils are 2-4 nm wide and form 20-100 nm wide aggregates, somewhat wider than those of plant-based microfibrils. Another difference to plant-based fibrils is that BC contains no hemicelluloses, lignin or extractives and once the bacteria have been removed, the end-product is highly pure cellulose (Kangas 2014).

Bacterial cellulose has several commercial uses in pharmaceuticals and food industry. Its high water holding capacity makes it ideal for burn wound dressings keeping the wound moist while at the same time absorbing excess tissue fluids, alleviating pain and reducing scar tissue formation. BC can be moulded into various shapes, for example glove-like, already in the cultivation phase. Bacterial cellulose is biocompatible and its ability to promote tissue growth makes it suitable for tissue engineering scaffolds besides wound dressings (Czaja, Krystynowicz et al. 2007, Dugan, Gough et al. 2013). In the Philippines, *nata de coco* is a traditional dessert produced by fermentation of coconut water into a nanocellulose suspension by *Acetobacter xylinum* (Halib, Amin et al. 2012).

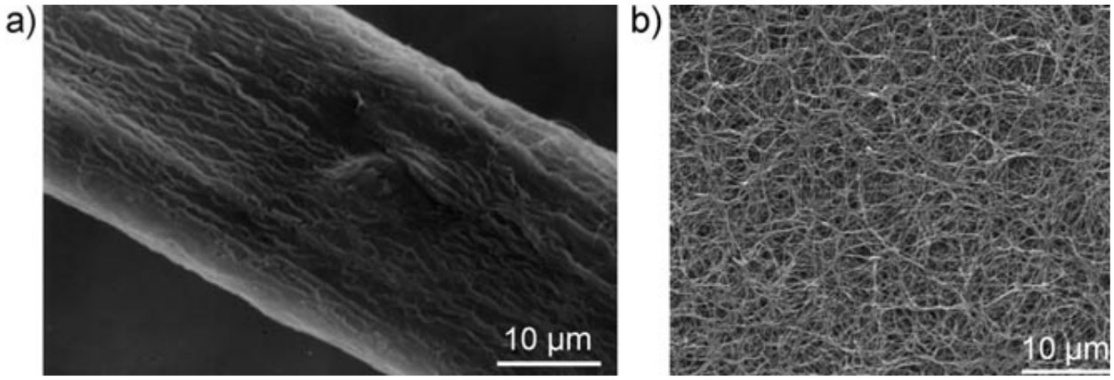

Figure 9. Electron micrographs of fibres of a) common pulp from plant cellulose and b) bacterial cellulose (Klemm et al. 2011).

4. Production of microfibrillated cellulose

This chapter discusses the various production methods for microfibrillated cellulose. Laboratory methods, like homogenization and cryocrushing, and pre-treatments are covered briefly with the focus on refining without chemical or enzymatic treatments.

Chemical pulp seems to be the most common source for microfibrillated cellulose as it has been used by Taipale et al. (2010), Janardhnan & Sain (2007), Laine et al. (2004), and many others. In some experiments dissolving pulp (Yamauchi, Amano 2014), recycled pulp (Spence et al. 2010), and mechanical pulp (Laleg, Hua 2011) have been used as well. If MFC production is integrated to a pulp mill, it is possible to use other pulp streams in the process than the end-product going to paper mill. Spence et al. (2011) argue that residual lignin and hemicelluloses enhance fibrillation by blocking some of the cellulose fibrils from bonding with each other. They found that unbleached pulp provided better MFC in the terms of elastic modulus, tensile strength, toughness, and SSA compared to bleached pulp. Similar results were reported by Desmaisons et al. (2017). The team found that MFC made of pulp containing 15 % of hemicelluloses was significantly better than another MFC produced from pulp with no hemicelluloses. However, other variables than hemicellulose content between the pulps in question might have contributed to the difference. Depending on the MFC concentration and its dispersedness, unbleached MFC could have a negative impact on the brightness of the paper. Nevertheless, if MFC is used e.g. in a cartonboard middle layer, optical properties are irrelevant.

4.1 Pre-treatments

Main drawback of MFC has been the highly energy intensive manufacture. Several attempts to tackle this problem with enzymatic, chemical and mechanical pre-treatments have been made (Ankerfors 2015, Tozluoglu, Poyraz 2016, Janardhnan, Sain 2007). The key function of any pre-treatment is to loosen the fibre structure and break hydrogen bonding between microfibrils. Henriksson et al. (2007) argued, that mechanical manufacture of MFC without pre-treatment damages the microfibril structure, reduce the

degree of polymerization and crystallinity, and the end-product often falls short of the desired level of fibrillation.

In an experiment by Ankerfors (2015), enzyme treatment or carboxymethylation of cellulose prior to microfluidization reduced the energy consumption significantly. Best results were obtained by carboxymethylation that decreased the energy consumption up to 90 %. The authors believed that further improvements to the process could drop the energy consumption by 98 % to 555 kWh/t. Tejado et al. (2012) combined data from several publications and found that energy consumption in MFC production was reduced logarithmically to one tenth with increasing carboxyl group content, energy consumption approaching zero at around 3 mmol/g content. However, commercial success of using carboxymethylated cellulose for MFC production is questionable, since the process involves two ion exchanges, two-hour CMC treatment in high temperature and washing with de-ionized water.

Enzymes for the pre-treatment of pulp can be extracted from fungi and bacteria. Several enzymes with individual functionalities exist and they are generally referred to as cellulases (Santangelo 2011). Varying results from enzymatic pre-treatments have been obtained. Janardhan & Sain (2007) used an enzyme extracted from Dutch Elm disease inflicting fungi. They achieved enhanced fibrillation with the pre-treatment with little or no undesirable damage to the fibrils. However, in another attempt, a combination of PFI refining and cryocrushing proved so effective that enzymatic pre-treatment had no noticeable impact on the end-product.

Henriksson et al. (2007) compared acid hydrolysis and c-type endoglucanase as a pre-treatment for homogenization. Both pre-treatments lowered the energy consumption significantly. Enzyme treatment produced stronger, smaller and more uniform fibril aggregates compared to the acid hydrolysis. The team suggested that the enzyme works by promoting cell wall swelling.

Mechanical pre-treatment is typically done by a normal pulp refiner (Heiskanen, Kastinen et al. 2016, Amiri, Dorris et al. 2012) or a laboratory beater (Henriksson, Berglund et al. 2008). Abe et al. (2007) used wood powder as their raw material for nanocellulose. Mechanical pre-treatment can be used to prevent clogging or other process failures by e.g. reducing the fibre length.

Oxidation is another pre-treatment method used to reduce the energy consumption of cellulose fibrillation. Usually done by (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl, commonly known as TEMPO, oxidation depolymerizes cellulose in a similar way as strong acids. Ozone can also be used instead of TEMPO (Bilodeau, Paradis 2013).

4.2 Refining

Refining, or beating, is the repeated mechanical treatment of cellulosic pulp inflicting pressure, shear forces, and cutting on fibres (Kainulainen et al. 1998). Main purpose of refining is to enhance paper strength by promoting conformability and bonding of individual fibres. One effect of fibre cutting is the improvement of formation especially with long-fibre softwood pulps. Refining is a complicated process and more research is needed to better understand what happens to individual fibres, how the shape and number of blades, blade gap and rotation speed affect them and what are the probabilities for individual fibres to receive certain treatment. As crucial as the refiner parameters are the properties of the fibre - wood species, seasonal changes, pulping, and hornification all impact the end results. Refiners are typically divided into conical and disc refiners (Koskenhely 2008, Maloney 2018).

4.2.1 Refining in papermaking

Traditionally, refining was done by Hollander beaters and their kind, hence the term “beating”. Beaters’ impact on the fibres was easier to control and they produced more homogeneous pulp than modern commercial refiners, but the limited operating speed and scalability led to the abandonment of beaters. Modern refiners are controlled more or less exclusively by adjusting the refining energy. A feedback loop between the strength

of vacuum at couch and refining energy is typical. This way the adjustments are always somewhat late and have little regard to the full effect of refining (Koskenhely 2008, Maloney 2018).

Refining works in several ways. Pressure type stress promotes internal fibrillation loosening fibre structure and increasing swelling and conformability. Conformability, fibres' ability to bend and match each other's shape, leads to a denser, more connected structure of a paper. Shearing forces cause external fibrillation, the partial removal of fibre cell wall. External fibrils have high water holding capacity, promote bonding and make sheets more consolidated and smooth. Shearing also produces fines. Refining does not affect micropores, but notable increase in macropore volume has been demonstrated (Laine et al., 2004), probably due to both internal and external fibrillation. Other impacts of refining include fibre length reduction by cutting, creation of kinks and dislocations, loss of bulk and straightening or curling of fibres depending on the refining characteristics. These phenomena affect pulp's water holding capacity as well as mechanical and optical properties. Generally speaking, as the mechanical properties improve, optical properties deteriorate and water removal becomes harder (Kainulainen et al. 1998, Koskenhely 2008).

4.2.2 Theories on refining

Adapted from Erik Sjöström's work

Chemical pulp refining is typically done in low consistency (LC). LC refining refers to range of 2 % to 6 % of bone dry fibres in water. As the pulp is refined between the bars on the stator and the rotor of a disc or conical refiner, both mechanical and hydraulic forces are at work. Stress treatments, such as crushing, bending, pulling and pushing of fibre clumps, occur between the bypassing bars (Figure 10). Rolling, twisting, and other shear stresses take effect in the grooves (Smook, 1992).

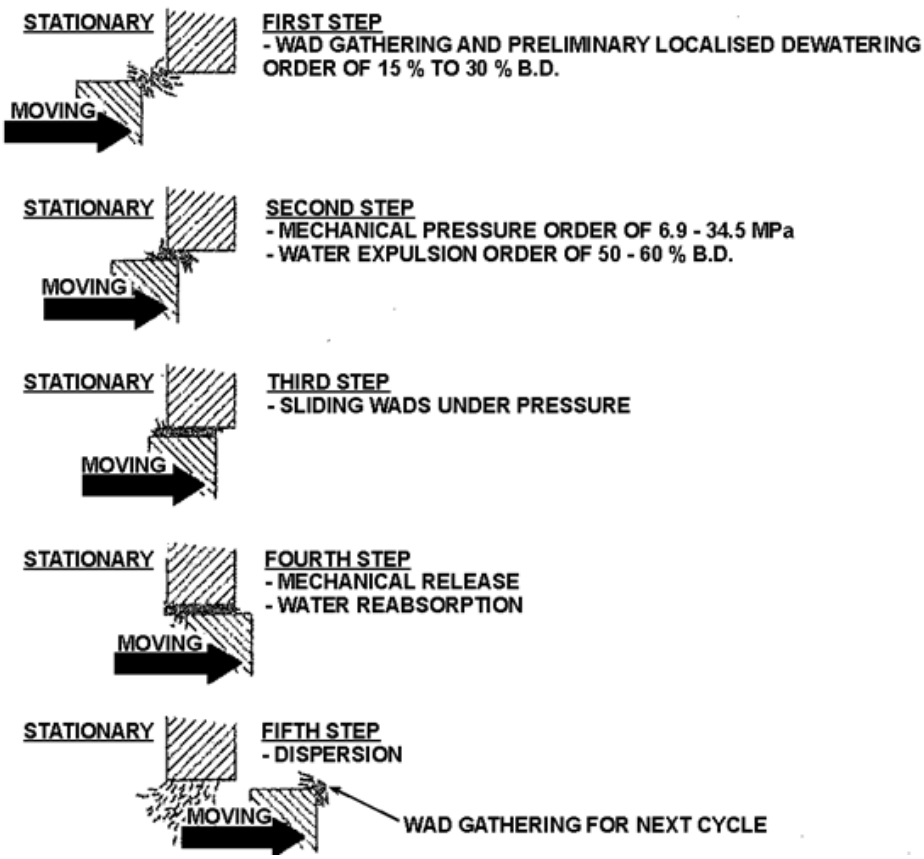

Figure 10. Illustration of refining between two bars (Smook, Kocurek 1982).

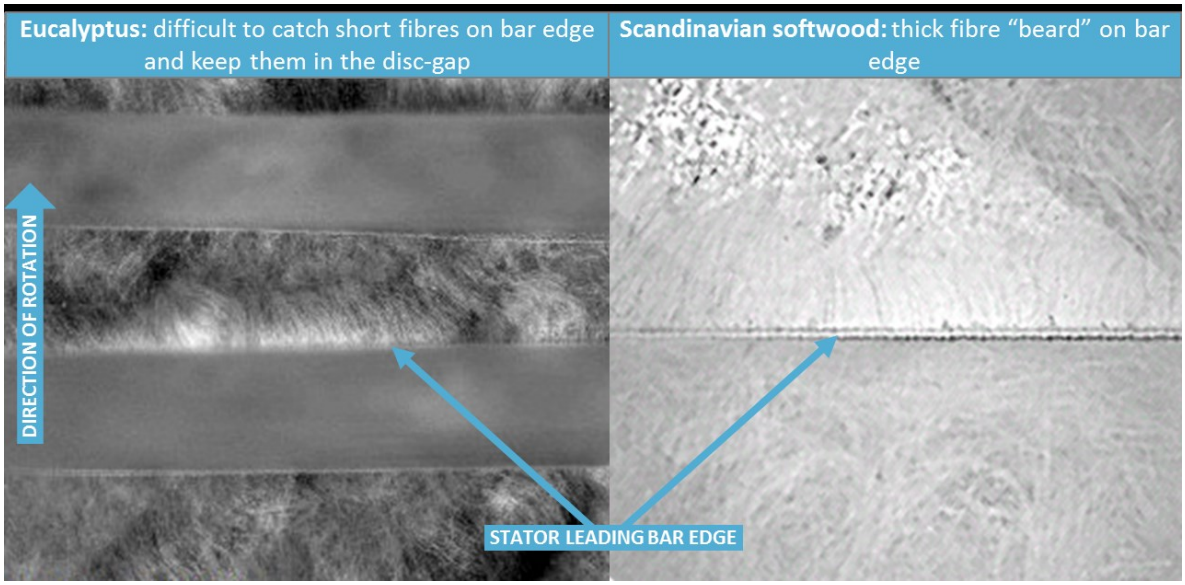

Figure 11. Laser pulse image through stator window with ProLab™ laboratory refiner (JiMing, Sjöström 2012).

Too intense refining leads to fibre cutting. Short fibres do not flock so well onto the refiner bars (Figure 11) resulting in less fibrillated pulp. Same happens when the refining consistency is too low. In a study by Lundin et al. (2008), bar trapping factor was reduced

by 80 % when the consistency was changed from 4 % to 2 %. This meant that less fibres were gathered into a floc on an advancing rotor bar leading to high increase in refining intensity and overall reduction in refining efficiency. Though fibre cutting is mainly avoided today, some mills purposely induce fibre cutting to enhance absorbency, porosity, and optical properties for certain paper grades (Paulapuro 2008, Lumiainen 1998).

Refining is controlled by monitoring energy input per weight unit of pulp, called the specific energy consumption (SEC) and clarified in the Equation 1. SEC describes the net value of power used on fibres during refining (Lundin et al. 2008). To calculate the net power, idle power is subtracted from the total power consumption. Idle power is determined by running water through the refiner with fillings fully parted from each other. Rotation speed, filling pattern, direction of rotation, and water flow regulated by the pump all affect the idle power (Baker 2000).

Equation 1. Specific energy consumption.

$$SEC = \frac{P_{tot} - P_0}{\dot{V}C} \left(\frac{kwh}{t}\right)$$

Where

$P_{tot} =$ Total power consumption (kWh),

$P_0 =$ Idle power(kWh),

$\dot{V} =$ Flow $\left(\frac{l}{h}\right)$,

C = concentration of pulp in water $\left(\frac{t}{l}\right)$.

Specific edge load (SEL, Equation 2) theory is the most common method used to describe refining intensity (Kerekes 2011). Developed by Walter Brecht and Wolfgang Siewert in 1966 from the work of Ferdinand Wultsch and Wolfgang Flucher in 1958, SEL is determined by dividing the net power intake by cutting edge length (CEL, Equation 3) multiplied by rotation speed.

Equation 2. Specific edge load.

$$SEL = \frac{P_{tot} - P_0}{nCEL} \left(\frac{J}{m}\right)$$

Where

n = rotation speed $\left(\frac{1}{s}\right)$ or $\left(\frac{rev}{s}\right)$,

CEL = cutting edge length $\left(\frac{m}{rev}\right)$.

Equation 3. Cutting edge length.

$$CEL = z_r z_s \bar{l} \left(\frac{m}{rev}\right)$$

Where

z = Bar amount on filling,

$\bar{l}$ = Average length of bars (m) or $\left(\frac{m}{rev}\right)$.

SEL does not account for the heterogeneity of natural fibres and assumes the load and fibres to be evenly distributed along the bars of the fillings. However, as an easily applicable and reasonably good estimate of the refining intensity it sees wide use in the industry in choosing the correct refiner size and filling pattern (Kerekes 2011, Paulapuro 2008, Baker 2000). Starting in 1990, Lumiainen further developed the theory by introducing specific surface load (SSL) and number of refining impacts (Lumiainen 1998). Taking bar width into account, specific refining energy (SRE) can be calculated as illustrated in the Equation 4.

Equation 4. Specific refining energy.

$$SRE = IN \times SSL \times IL$$

Where

SRE = specific refining energy $\left(\frac{kJ}{kg}\right)$,

IN = the amount of refining impacts $\left(\frac{km}{kg}\right)$,

SSL = the specific surface load $\left(\frac{J}{m^2}\right)$,

IL = the bar width factor (m).

The IN tells a number of generated refining impacts for a mass flow pass through the refiner (Equation 5).

Equation 5. Amount of refining impacts.

$$\mathrm{IN} = \frac{\mathrm{L_s}}{\mathrm{M}}$$

Where

$\mathrm{L_s} = \text{cutting speed of the bars},$

$\mathrm{M} = \text{fiber flow } \left(\frac{\mathrm{kg}}{\mathrm{s}}\right)$

The SSL factor is obtained by dividing the SEL value by the width factor IL (Equation 6, Equation 7).

Equation 6. Specific surface load.

$$\mathrm{SSL} = \frac{\mathrm{SEL}}{\mathrm{IL}}$$

Equation 7. Bar width factor.

$$\mathrm{IL} = \frac{\mathrm{w_{b,r}} + \mathrm{w_{b,s}}}{2} \cdot \frac{1}{\cos\left(\frac{\alpha}{2}\right)}$$

Where

w = is the bar width,

α = average intersecting angle.

SSL theory provides notable improvements to SEL theory, yet leaves out important factors such as filling grooves, wear of filling, and the length of fibres (Paulapuro 2008). The most rigorous theory in use was developed by Richard Kerekes in 1990. His 31 equations consider density of water, pulp consistency, fibre length, number of bars, rotational speed, gap clearance, width and depth of grooves, bar angle, inner radius, refining zone length, and refiner angle, collectively referred to as C-factor. Kerekes developed separate C-factors for conical and disc refiners. Energy used on the pulp is determined by

combining the C-factor with mass flow and net power intake (Cuberos-Martinez, Park 2012).

4.2.3 Fines

Fines have very similar effects in the fibre network as external fibrillation or microfibrillated cellulose. Indeed, the effect of external fibrillation on paper strength has been studied by the addition of MFC (Kang, Paulapuro 2006). The large SSA promotes swelling and bonding and inhibits water removal. Fines, fibre fragments and other small particles, are counted as the fraction of pulp that goes through a 100- or a 200-mesh, usually several micrometres in size. In chemical pulp, fines are divided into primary fines containing ray and parenchyma cells readily present in pulp, and secondary fines, fibre wall particles, produced by refining. The chemical composition, namely the ratio of carbohydrates and lignin, of fines is close to that of the pulp it is originated from with slight differences. In chemical pulp, the share of hemicelluloses is somewhat greater and in mechanical pulp, lignin content is higher in fines than in the fibres. The share of fines varies profoundly and is related to the type and intensity of refining. In the average, chemical pulp contains around 10 % of fines and mechanical pulp some 30 % (Kainulainen et al. 1998, Taipale et al. 2010).

4.2.4 Research on microfibrillated cellulose production by refining

In the academic literature, references to refining as the production method for MFC are scarce. However, the widely used Masuko Supermasscolloider (Abe et al. 2007, Taipale et al. 2010, Kang, Paulapuro 2006, Nair, Zhu et al. 2014, UMaine 2018), referred to as a micro-grinder or as an ultra-fine friction grinder, has similar operational principle as a disk refiner. In a Masuko grinder, two ceramic disks separated by a tiny gap are used as stator and rotor. Operation with adjustable gap clearance and rotating speed is equivalent to disk refiners (Masuko 2018, Koskenhely 2008). In a sense, micro-grinding or friction grinding can be considered as refining. Differences between the two lie in the controlling system and disk surface. Conventional refiners are primarily controlled by adjusting the energy consumption i.e. the refiner load (Koskenhely 2008), whereas Masuko is controlled by gap clearance (Maloney 2018). Masuko uses grindstones instead of disks

with blades and grooves. Still, the difference between grinding and refining is small compared to homogenization, microfluidization, or cryocrushing.

As the pulp approaches a gel-like, microfibrillated state, refiner plates must come to a very close proximity within each other for any further fibrillation to take place. Thus, the risk for clashing and blade damage increases. Controlling refining only by the energy intake does not suffice with MFC production and more sophisticated controlling system is required. Typically, the vibration induced by the two plates closing in on each other is monitored, and this parameter should be observed closely when refining beyond normal papermaking needs.

Nair et al. (2014) studied the gradual effects of Masuko grinding for bleached softwood kraft pulp. The pulp was fed continuously to the device for six hours. First 15 to 30 minutes, or around 10 passes, increased the density dramatically. However, SEM characterization revealed that fibrillation was very heterogeneous and much of the fibres were left intact. Additional passes through the grinder ensured more uniform treatment. After two hours, or some 25 passes, the variations in fibrillation became negligible. Two hours of grinding required little under 5 000 kWh/t of energy. From two to six hours, no detectable changes in morphology were observed. Increase in tensile strength and stress strain was near linear until two hours after which a levelling off was noted. After four hours, the mechanical properties started to deteriorate.

Without an exception, the production of MFC seems to require multiple passes through a refiner or a grinder. Using multiple passes requires a circular flow or several refiners in series (Cerealus 2011, Amiri et al. 2012, Bilodeau, Paradis 2015). If a circular flow is used, a hydrocyclone or some other screening method could be useful for separating finished MFC from rest of the pulp (Madani, Kiiskinen et al. 2011). Using multiple refiners has the advantage that each one can be optimized for the fibrillation state of the pulp passing through at that point. Refiner filling design, gap clearance, and refiner load can be adjusted. Of course, more space and investment capital are needed as well. Masuko seems to require up to several tens of passes for sufficient fibrillation to take place (Kang,

Paulapuro 2006, Gane, Schenker et al. 2011b) consuming huge amounts of energy. The lowest energy consumption for MFC produced by Masuko found was 1500 kWh/t (Spence et al. 2011). With the current energy prices, it would mean approximately 100 €/t on top of the price of pulp (IEA 2016), which is a commercially viable figure. However, figures one order of magnitude higher have also been suggested (Nair et al. 2014).

4.2.5 Commercial MFC production concepts utilizing refining

In contrary to the academia, many patents and patent applications present refiners as the means for MFC production (Heiskanen et al. 2016, Amiri et al. 2012, Gane, Schenker et al. 2011a, Gane et al. 2011b, Björkqvist, Koskinen et al. 2011, Husband, Svending et al. 2010a, Husband, Svending et al. 2010b, Suzuki, Hattori 2003, Weibel, Paul 1993). Achieving nanoscale fibrillation with a refiner requires multiple passes from less than ten up to as high as 90 (Suzuki, Hattori 2003). MFC refiners seem to be operated primarily at low, 1-6 % consistencies (Björkqvist et al. 2011, Suzuki, Hattori 2003). MFC refiners differ from pulp refiners by having reduced blade height of e.g. 2-3 mm compared to 6-10 mm used in papermaking (Heiskanen et al. 2016).

FiberLean®, a joint venture between Imerys and Omya, is a commercially available MFC production concept. MFC is produced by refiners in the presence of a mineral filler. The two companies claim that the filler facilitates grinding by transferring mechanical energy to the fibres (FiberLean 2016). In a 2011 patent application by Omya, Gane et al. describe a method utilizing Masuko grinder. Though the energy consumption was not disclosed, 13 passes through the grinder do not suggest huge energy savings by the addition of a filler in the fibrillation phase. No pre-treatment is used in the FiberLean method and the filler in use can be PCC, kaolin, talc, graphite, or any other common papermaking mineral additive. Other related patents (Husband et al. 2010b, Husband et al. 2010a, Gane et al. 2011a) present homogenization and a tower mill as alternatives to disc refining. Though FiberLean is said to be robust and reliable, the hard mineral particles probably take their toll on the condition of the refiner.

Canadian research and development organization FPInnovations has a patented production method for cellulose filaments (Amiri et al. 2012, Dorris, Ben et al. 2013). The organization teamed up with Kruger in 2013 to build the first 5 tons per day demonstration plant producing cellulose filaments under the tradename FiloCell™ (Kruger 2015). Cellulose filaments are essentially microfibrillated cellulose, though FiloCell™ is claimed to have the highest aspect ratio in the market. Indeed, the patents describe a product 30-500 nm wide and up to 350 microns long. With these dimensions, FiloCell™ seems to lie somewhere between microcellulose and well refined pulp. FPInnovations has filed several patents for the production of cellulose filaments, and it is unclear, which method is actually used at the demonstration plant. Method by Hua et al. (2011) utilizes blades rotating at high speed. In another case, the manufacture is carried out by high consistency refining with a total energy consumption between 5 000-20 000 kWh/t. Patent filed in 2012 (Amiri et al.) describes two refining routes:

1) "8 passes at 900 rpm using a 36" double disc refiner with a standard Bauer disc pattern 36104 at 30 % consistency using bleached softwood kraft pulp as raw material
2) one pass at 1800 rpm with a 22" pressurized refiner using Andritz 0170002 16-plate pattern followed by the procedure used in route 1) using black spruce wood chips as raw material."

FiloCell™ can be dried and redispersed and thus sold outside the plant. It is unclear how dry the product really is, and how and to what degree the redispersability is achieved since no chemicals or derivatisation to suppress hydrogen bonding upon drying is used. Quite possibly the larger dimensions compared to ordinary MFC help with dispersion. Still, redispersable MFC is not out of ordinary. UPM has several patents for processes of drying MFC using organic solvents (Laukkanen, Teirfolk, Nuopponen, Walther et al. 2012, Laukkanen, Teirfolk et al. 2012) or by heated airflow (Hillebrand, Nuopponen et al. 2013). In the latter process a solids content of 20-50 % is reached, and anionic modification of the cellulose surface and addition of cationic starch are utilized to achieve redispersability.

The University of Maine has worked on several scalable CNF production methods. FibreFine™, a cooperation with GL&V, utilizes standard papermaking equipment (GL&V 2017). Pulp is circulated several times through a disc refiner with a special plate design and an anti-clash protection for the plates (Williamson 2014). Endpoint is measured by fines level. A 1 t/d demonstration plant is running at the University of Maine, and in May 2015, Paperlogic acquired a 2 t/d plant from GL&V (Miller 2015). A 20 t/d demonstration plant with refiners in parallel and in series with each other has been designed. A mobile demonstration refiner is available for test runs at a mill in The United States. Though the total energy consumption has not been disclosed, some indicative values can be cautiously deducted from a GL&V presentation available at SPCI's (Swedish pulp and paper engineers' association) web page (Sundin 2018). The presentation describes "a process to manufacture Cellulose Nano-Fibrils (CNF) using only mechanical energy at a total cost of less than 2 000 €/ton". Even if the price of pulp is included, 2 000 €/t would mean over 10 000 kWh/t even with a high cost of energy (IEA 2016).

Another University of Maine based technology, Cerenano®, uses chemical treatment to reduce the energy consumption (Cerealus 2011). Fibrillation is achieved by 13" and 20" refiners in series. After fibrillation, CNF is blended with cooked starch and chemically treated in the presence of steam. Total energy consumption or whether the fibres are recirculated through the refiners has not been disclosed.

Bilodeau et al. (2016, 2015, 2013) from The University of Maine have filed patent applications related to production of nanofibrillated cellulose from Kraft pulp. The applications from 2016 and 2015 describe refining methods that yield pulp with 2-30 % CNF content. It is debatable whether these methods can really be considered as micro- or nanocellulose manufacture since refined chemical pulp always contains some amount of fines, typically around 10 % (Kainulainen et al. 1998). The patent applications propose fines level as a measurement for CNF concentration, hence no distinction between nanocellulose and fines is made. Though there are similarities in these applications to FibreFine™ and Cerenano®, definite connections of these patents to the commercial technologies cannot be concluded.

Stora Enso has announced the use of MFC together with CTMP in liquid packaging (Mäkinen 2017). In liquid packaging board (LPB), CTMP is used as a middle layer for improved stiffness due to high bulk. Chemical pulp or other binding material is needed to prevent internal cohesion breakage in the CTMP layer and the delamination from top and bottom layers in LPB. MFC is an efficient binding material and can potentially provide the required internal bond strength with much smaller quantities than ordinary kraft pulp. Other commercial, continuous MFC production systems have been developed or announced by Borregaard (Exilva MFC), SAPPI, Innventia in cooperation with BillerudKorsnäs, Verso Paper, joint venture between Resolute Forest Products and Mercer, American Process, Nippon Paper, French research institutes CTP and FCBA, Oji Paper, UPM, and VTT (Williamson 2014, Kangas 2014, Ankerfors 2015, Miller 2014).

4.3 Other manufacturing methods

Homogenization was the first method used to produce MFC, introduced by Turbak et al. (1981) and Herrick (1983). In homogenization (Figure 12), a low consistency suspension is forced with high pressure through a narrow passage[1]. The suspension then collides to a controllable valve[2] and is subsequently allowed to a chamber[3] causing rapid drop in pressure, usually as high as 60 MPa. After repeated passes through the device, the high shear, cavitation, and impact forces disintegrate cellulose into nano- and microscale fibrils (Turbak et al. 1981). Problems reported with homogenization include extremely high energy consumption of up to 27 000 kWh/t, clogging of the device, non-scalability, and heterogeneous end-product (Ankerfors 2015, Spence et al. 2011, Ankerfors, Lindström et al. 2007, Suzuki, Hattori 2003). Various pre-treatments can be used to reduce the energy consumption and to produce more uniform MFC (Henriksson et al. 2008, Ankerfors et al. 2007).

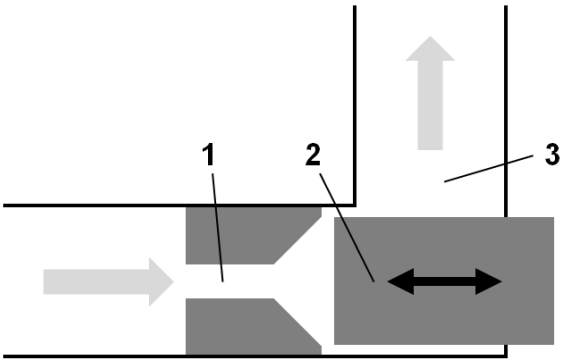

Figure 12. Operational principle of a homogenizer.

Microfluidizer is similar to a homogenizer and is sometimes referred to as a one type of a homogenizer (Henriksson et al. 2008). Figure 13 illustrates the operational principle of a microfluidizer. Particle size is diminished by passing the dispersion with high pressure through a combination of high shear zones[1] and high impact zones[2]. Unlike a homogenizer, a microfluidizer has no moving parts and clogging can be resolved by using reverse flow. A microfluidizer, operating at a constant shear rate, enables better control of the processing intensity than homogenizers operating at constant processing volume. The chamber geometry can be designed for specific materials and particle dimensions (Spence et al. 2011, Microfluidics 2018). Remarkably, energy consumptions of even one order of magnitude lower than for homogenizers have been reported with microfluidizers, regardless of the similarities between the two processes (Spence et al. 2011).

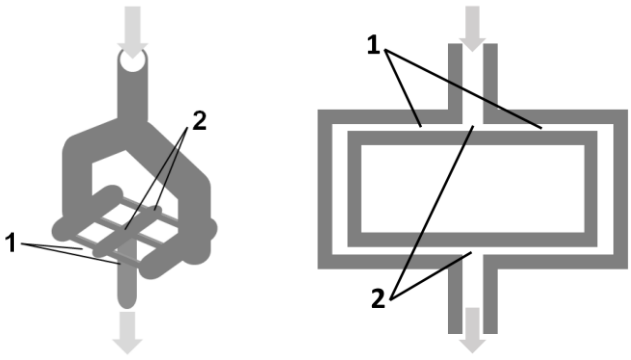

Figure 13. Operational principle of a microfluidizer.

Spence et al. (2011) compared the energy consumption and resulting mechanical properties of MFC prepared by refining with a Masuko grinder, microfluidization, and homogenization. The energy consumptions were 1 600 kWh/t, 2 900 kWh/t, and 21 900 kWh/t, respectively. The highest tensile strength was achieved by microfluidization and highest elastic modulus by homogenization. However, by far the most cost efficient method was refining without any pre-treatment. Compared to the microfluidized MFC, the tensile index value was similar, elastic modulus around 15 % lower, and specific surface area considerably higher with half the price. Furthermore, Spence et al. reported that refining caused no clogging unlike the other two methods. Disadvantage with refining is the inevitable wear of fillings.

*Table 2. Comparison between various manufacturing methods (Spence et al. 2011) *) no pre-treatment, **) indicative energy price with 60 €/MWh.*

	TEC [kWh/t]	Price** [€/t]	SSA [m^2/g]	E [MPa]	TI [Nm/g]
Original fibres	-	-	5	2 500	30
Pre-treated fibres	2 000	120	25	5 800	70
Refiner*	1 600	90	60	4 600	110
Refiner	3 600	210	45	4 400	90
Microfluidizer	2 900	180	40	5 400	120
Homogenizer	21 900	1 310	70	6 300	90

Cryocrushing and ball milling (Chakraborty 2005, Zhang et al. 2015) are other reported processes for MFC production. However, scaling up and feasibility of these methods is questionable. For the meantime, they remain a laboratory curiosity more than a potential commercial production method to be reckoned with.

5. Applications of microfibrillated cellulose

While scientific literature concentrates more on composites and various high-value applications in e.g. biomedicals, papermaking should offer the largest market potential for MFC. With the current disclosed MFC and CNF production in several tens of tonnes at maximum globally (Kangas 2014), the growth potential is immense. In many applications, the market size, hydrophilicity or heterogeneity of cellulose, the price of micro- and nanofibrillated cellulose, or the fact that the needed concentration is very small restricts the market potential. As is natural considering the scope of this thesis and the market distribution, this chapter concentrates on papermaking with a brief introduction to other applications.

It should be noted that while the scientific literature and patents use terms CNF and MFC crosswise, here only the term MFC is used to avoid misapprehensions. Standard nomenclature is still under development (TAPPI 2015) and there is seldom enough information about the characteristics of the fibrillated product in question to determine whether it should be classified as MFC or CNF.

5.1 Microfibrillated cellulose in papermaking

Paper constitutes of fibres, fines, fillers, and additives, such as microfibrillated cellulose (MFC). The fibres, forming an interconnected network, have an intrinsic tendency to bond with each other. In papermaking, cellulose fibres are subjected to cutting, drying, stretching, pressing, and shearing that all affect the bonding, structure, and orientation of fibres and ultimately the mechanical and optical properties of the end-product. Additionally, wood species, type of pulping, bleaching, and refining all play a role in the properties of finished paper.

In papermaking, MFC can be used as a barrier or coating, but the most promising applications are as wet-end additives for improved strength properties, retention, and formation. The high surface area of MFC improves inter-fibre bonds promoting paper dry strength, internal bond strength, and wet strength at wire. Addition of MFC can yield

products with similar or better mechanical properties with less fibre. Lighter paper or board means savings in manufacture, transportation, and end-use. Depending on the bottlenecks of a given mill, using MFC can increase the production capacity. Enhancing the strength with MFC also enables higher share of fillers that are cheaper than fibre and give better optical properties (Ankerfors 2015, Hassan, Hassan et al. 2011, J. Laine, Österberg et al. 2010, Sundin 2018). Multilayer cartonboards are among the most promising product categories for the utilization of MFC. Chemical pulp is traditionally used as a binding material in the bulky middle layer. MFC can increase the bonding of the fibre network with much lower share than chemical pulp enabling higher share of cheaper and bulkier TMP.

Taipale et al. (2010) observed a linear increase in drainage resistance, tensile strength, and internal bond strength of a paper with increasing MFC content. MFC's high affinity to water elevates drainage resistance while tensile strength is promoted by the increasing number of bonds and mechanical entanglement. Internal bond strength reached a maximum value at a MFC content of 4.5 % after which it started to level off. This phenomenon is thought to correspond to formation of delamination planes creating low-energy fracture paths with higher MFC content. Taipale and his team (2010) concluded an optimal MFC content to be around 3 %. With this concentration, a significant improvement in strength properties without a severe increase in drainage resistance was observed.

Ankerfors et al. (2015) found that by adding 5 % MFC and 2 % cationic starch (CS), the filler content of the paper, produced by a pilot machine, could be increased from 20 % to 33 %. Higher filler content alleviated the water removal more than MFC inhibited it. Both mechanical properties and retention of the paper were enhanced. In the same experiment, MFC alone was found to decrease retention when used with common retention aid. The authors suspected that MFC bonded with the retention aid, thus inactivating them both to some degree. Ankerfors et al. (2015) noted that these findings are in contrary to earlier laboratory research and that the higher shear forces of pilot paper machine compared to laboratory equipment could be the reason. The best results

overall were achieved by MFC and CS together as opposed to using only one of them. It seems that these two polymers work best together, as similar results have been published by Taipale et al (2010), Kosonen & Kajanto (2012), Laleg & Hua (2011), Håkansson & Heiskanen (2017), and Paltakari et al. (2010). Ankerfors and his team also found that linting and dusting of newsprint can be greatly reduced using approximately 1 g/m^2 of MFC at the size press. Adding anionic starch to the mixture provided further improvement.

Kosonen and Kajanto (2012) studied the paper-reinforcement effect of MFC on a high-speed pilot machine. Only 1-2 % of MFC with 1 % of cationic starch increased the tensile strength significantly enabling a 10-15 % reduction in grammage with a mix of hardwood and softwood kraft pulp. MFC-reinforced paper had slightly lower scattering coefficient and thus lower opacity compared to the control. Paper was denser leading to decreased air permeability. Dewatering was reduced a little, but after wet pressing the solids content was even higher with than without MFC. Total retention remained constant. The findings of Kosonen and Kajanto (2012) indicate that MFC can have significant impact on paper properties and wet-end functions even at relatively low concentrations.

González et al. (2012) compared refining and addition of MFC to the properties of printing and writing paper made of bleached eucalyptus kraft pulp. The team used much higher concentrations compared to Kosonen and Kajanto (2012). However, the two studies cannot be directly compared to each other as other was conducted with laboratory equipment and the other one with a pilot machine, and different characterization techniques were used. Adding MFC to non-refined pulp produced paper with higher drainage resistance and similar mechanical properties compared to well-refined pulp without MFC. Best mechanical properties were achieved with 6 % and 9 % MFC load, though the drainage resistance grew stronger with increasing share of MFC. 0.5 % of cationic starch was used as a retention aid.

As can be seen, MFC load in different experiments varies profoundly. In some studies, significant strength enhancement has been reported with only 1 % load (Kajanto,

Kosonen 2012), while Hassan et al. (2011) used MFC contents up to 50 %. Clearly, a very different MFC product is used in these two studies. Also, the choices researchers make concerning which properties are measured and which not affect the apparent outcome. Tozluoglu & Poyraz (2016) report significant reduction in tear strength, optical properties, and water drainage with 1.5-3 % MFC load, while at the same time tensile strength and burst strength increased profoundly. Refining characteristics of pulp, its ionic strength, pH, and wet-end chemistry also make the optimal MFC content highly case-specific.

Several companies operating in papermaking business are producing MFC for commercial or semi-commercial purposes, including Stora Enso, UPM, Borregaard, Norske Skog, Oji Fibre Solutions, Nippon Paper, J. Rettenmaier & Söhne, Kruger, SAPPI, BillerudKorsnäs, Verso Paper, Resolute Forest Products in cooperation with Mercer, Omya, and Imerys (Ankerfors 2015, Williamson 2014, Kangas 2014, Miller 2014). The disclosed annual capacities are typically in the range of 100 to 500 tonnes and 2 000 tonnes at maximum.

5.1.1 Challenges with microfibrillated cellulose

Extremely high viscosity makes MFC hard to pump and disperse, meaning more water and thus more pumping and drying is needed. Pressability and clogging of equipment can also produce challenges. However, by optimizing the wet-end chemistry, the problems with drainage can be tackled as shown by Ankerfors et al. (2015). Significant shear thinning nature of MFC suspensions helps with the high viscosity (Karppinen, Saarinen et al. 2012, Kangas 2014). Reducing fibre length by pre-refining helps with clogging (Andresen et al. 2006).

Pulp has a tendency to form flocs even at consistencies below 1 %. Flocculation is increased with higher consistency and depends on basic fibre properties such as size distribution, dimensions, and flexibility (Gustafsson 2011). Same holds true for MFC suspensions, although the fibres are much shorter and have a higher aspect ratio. Karppinen et al. (2012) describe flocs at rest as “areas of higher density within a network”. Increased shear rate breaks this network gradually. Under flow, floc formulation is governed by cohesive forces, mainly van der Waals and electrostatic

interactions, number of collisions, and mechanical entanglement. Kraft pulp fibres are naturally slightly anionic, and increasing charge density decreases flocculation. At the same time, the wet web strength decreases. Also, the type of counterion present in the suspension affects these properties (Horvath, Lindström 2007).

MFC has similar negative impacts on paper optical properties as refining reducing opacity and brightness (Taipale et al. 2010). Another major challenge considering MFC is transportation. Shipping large amounts of water is not feasible and water removal is energy intensive and results in hornification. This problem can be avoided by producing MFC on-site.

5.1.2 MFC characterization for industrial applications

In order to predict the effects of MFC on the paper properties and the functions at the wet-end, the MFC in question must be characterized. SEM and AFM, though providing invaluable data in a laboratory environment, are not practical at a paper mill. Thus, indirect measurement techniques are used. Viscosity, fines fraction, fibre length, and turbidity indicate the degree of fibrillation and uniformity (Ankerfors 2015, Kangas 2014, Bilodeau, Paradis 2013, Kajanto, Kosonen 2012). Fibrillation increases viscosity, though fibril network properties, surface charge and colloidal particles affect viscosity as well. Fines fraction or fibre length could be measured by automated fibre image analyser similar to ones used in laboratories. A centrifugal screener letting the sufficiently fibrillated particles through and returning the residual back to the refiner could also be used. A “perfect” MFC with every particle at nanoscale would have zero turbidity as the visible light wavelength is around 400 nanometres at minimum. Turbidity might be hard to measure from a fast-flowing suspension, but other optical measurements such as light scattering could be used. In any case, the instruments already in commission such as vacuum strength indicators at the wire section should be used to evaluate the effects of MFC.

5.2 Other applications for microfibrillated cellulose

Interest in various nanomaterials, including nanoscale cellulose, arose in the 1970's with the development of novel physical and analytical methods for the characterization and production of them. Ever since, the number of publications and patents on micro- and nanocellulose has increased almost exponentially. Numerous potential applications for MFC have been proposed including construction, packaging, paints, rubber, concrete, ceramics, thermosets, thermoplastics, displays, panels, housings, foils, films, coatings, extrusion profiles, adhesives, food, barriers, wound-healing, insulation, membranes, and aerogels (Chinga-Carrasco 2013, Gane et al. 2011b, Liebner et al. 2010, Henriksson et al. 2008). The first commercial applications of MFC were as a thickener or emulsion stabilizer in the food industry (Turbak et al. 1981, Herrick 1983). Based on CAS (Chemical Abstracts Service) database, Kangas (2014) reports pharmaceuticals, reinforced plastics, textiles, and nonwovens the main application areas for MFC besides paper.

Microcellulose has many advantages in composite reinforcement. High aspect ratio, stiffness of cellulose crystals, easily modifiable surface, and of course biodegradability and renewability make the material an attractive option. The strength of cellulose in nanoscale is comparable to common technical materials such as glass, aluminium, and steel. In addition to reinforcing thermoplastics, nanoscale cellulose has applications in transparent displays, DNA-hybrid materials, adhesive reinforcement, hierarchical composites, and all-cellulose nanocomposites (Eichhorn et al. 2010). However, hydrophilic surface and affinity to water pose problems with cellulose-containing composites. A strong bonding with the often hydrophobic matrix is required, and any deformations due to water present in the material during processing or absorbed afterwards weaken the composite. Using unmodified cellulose with a thermoplastic matrix yields worse tensile and elongation properties compared to the matrix alone (Bledzki, Gassan 1999).

5.3 Rival materials

More intensive refining and the external fibrillation and fines produced by it can be considered a rival for MFC as a papermaking additive. Since the characteristics and role of fines and external fibrillation is discussed in the chapter *4.2 Refining*, this chapter concentrates on wet-end additives, namely cationic polyelectrolytes, that are used to achieve similar effects to MFC addition. In other applications, such as rheology modifiers in paints or reinforcement in composites, MFC competes with a set of wholly different materials. However, those applications are not in the scope of this thesis and are thus not included here.

5.3.1 Cationic polyelectrolytes

Cationic polyelectrolytes are common papermaking additives and most widely used one is cationic starch (CS) (Taipale 2010). Following benefits for cationic starch as a wet-end additive have been named: enhancing stiffness and bonding, improving formation, improving drainage, improving internal bonding and surface strength, improving wax-pick, increase dry strength properties, better writing and printing surface, reduced cost by allowing higher share of fillers or recycled fibre, enhanced runnability and productivity, and reduced energy consumption (Pulp Paper Mill 2013a, Pulp Paper Mill 2013b). Many of these enhancements are interconnected such as energy consumption and drainage or runnability and internal bonding. The list is very similar to the benefits of MFC, though CS has lower affinity to water and cationic surface enables electrostatic bonding in addition to hydrogen and van der Waals bonding. More bonding options enable more functionality, but the molecular weight of a cationic polyelectrolyte should be less than 10 000 g/mol or the functionality is impeded (J. Laine, Taipale et al. 2011, Taipale 2010).

According to Ankerfors et al. (2015), CS seems to be less effective than MFC as a dry strength additive. Direct comparisons between the strength enhancement potential of these two are scarce, and the findings of Retulainen and Nieminen (1996) challenge the results of Ankerfors and his team. The team found equal increase in kraft paper tensile strength with the addition of 1.2 % of CS as with the addition of 10 % of kraft fines. Retulainen and Nieminen (1996) investigated the strength enhancement mechanisms of

starch and fines in detail and found fundamental differences between the two. Fines were seen to work as structural strength enhancers increasing the bonded area and bearing load, both in the elastic and plastic regions. Starch was seen to work as a chemical additive increasing bond strength and stiffness of bond areas mainly in the plastic regions, thus making the fibre network stiffer and more brittle. The results considering the bonding phenomenon should be approached with certain reservation, as the bond strength was evaluated using Nordman bond strength, a method later found to be fundamentally flawed (Page 2002). By far the biggest increase in strength properties was achieved with the combination of fines and starch, as long as starch was added before fines. It was concluded that otherwise starch was adsorbed by fines instead of fibres. Hence, the increase in inter-fibre bond strength was lost. The methods for MFC reinforced paper described in the patents by Laine et al. (2010) and Paltakari et al. (2010) indicate similar findings. It should be noted that fines are highly heterogeneous material containing various residuals and having generally lower aspect ratio than MFC (Taipale 2010). Thus, MFC should be more effective strength enhancer than fines, even if the functionality is similar. Still, a 1.2 % to 10 % ratio indicates a significant difference in the strength enhancement. According to the work of Retulainen and Nieminen (1996), MFC would need to be over eight times more effective than fines to outweigh CS in tensile strength enhancement.

One of the main drawbacks with MFC, the increasing resistance to water removal, can be tackled by cationic polyelectrolytes that affect the fibre network structure and surface chemistry, promoting water removal (J. Laine et al. 2011). A challenge restricting the use of CS is its tendency to saturate the anionic charge of fibres. Once saturation is reached, retention of extra CS is poor leaving it circulating in the white water system. A substantial amount of CS also inhibits the retention of other cationic additives such as sizing and retention aids. Problems with runnability, microbiology and foaming can also occur (Axrup, Heiskanen et al. 2010).

Cationic starch is much cheaper than MFC having a price at a level of 500-700 €/t (Nurminen 2018). Price of MFC includes the cost of pulp that is at similar level than

cationic starch, and the cost of energy that starts from around 100 €/t as discussed earlier. Non-derivatised starch is a cheaper option for CS, but it has fewer functionalities compared to cationic starch. Other cationic polyelectrolytes include polybrene and polyacrylamides. Various mixtures can also be used.

Cationic polyelectrolytes do not only compete with MFC, as the best results with increased strength properties and water removal are reported with the combination of cationic starch and MFC (Retulainen, Nieminen 1996). Comparing the effects of additional refining, MFC and CS to drainage and paper strength, Taipale et a. (2010) found that the highest tensile strength was achieved by a combination of MFC and CS without reduction in drainage. In a patent by Laleg & Hua (2011), papers with filler content as high as 90 % were produced by replacing all or most of the pulp with MFC, precipitating calcium carbonate in the MFC suspension, and adding cationic starch and acrylic binders. A patent application by Stora Enso (Håkansson, Heiskanen 2017) for similar product, a paper with filler content up to 45 w-% produced by precipitating calcium carbonate in a MFC suspension, also mentions starch as an advisable additive.

5.3.2 Cellulose derivatives

Besides cationic polyelectrolytes, modification of the fibre surface, carboxymethyl cellulose (CMC), and various other chemicals can be used to enhance paper strength (Paltakari et al. 2010, Eriksen, Syverud et al. 2008). Hollertz et al. (2017) compared the effects of kraft MFC, carboxymethylated CNF, periodate-oxidated carboxymethylated CNF, and dopamine-grafted carboxymethylated CNF as paper strength additives. The non-derivatised reference, kraft MFC, was not fibrillated to the same extent as the derivatised products which should be taken into account in the comparison. At 15 w-% content, periodate CNF and kraft MFC had the highest retention and carboxymethylated CNF the poorest. Periodate CNF with a retention aid increased the tensile strength by 37 % and 89 % at 2 w-% and 15 w-%, respectively, compared to a reference having only the retention aid. Kraft MFC increased the tensile strength only slightly compared to the reference. Young's modulus was improved by approximately 40 % with addition of 15 w-% kraft MFC and by approximately 60 % with addition of 15 w-% periodate CNF. Generally, dopamine

CNF had similar strength enhancement compared to periodate CNF, and carboxymethylated CNF inferior strength enhancement compared to the other fibril materials. Wet tensile strength values up to 30 kNm/kg were achieved with periodate CNF, a significant improvement compared to the almost non-existent wet tensile strength of the reference. Derivatised fibrils did not increase the dewatering time as profoundly as kraft MFC. As a conclusion, cellulose derivatives seem to offer better strength enhancement properties with less problems in dewatering compared to non-derivatised fibrils. However, the expensive manufacture of cellulose derivatives reduces their attractiveness.

6. Conclusions on the literature review

As was hypothesised, refining appears to be the most feasible and reasonable method for continuous, commercial MFC production. Multiple patents and several articles support this conclusion. At least one research group has managed to produce suitable MFC with energy consumption at a level corresponding to around 100 €/t on top of the price of pulp. However, many others report much higher energy consumption levels, especially with larger refiners. This indicates refiner design and rigorous optimisation to be in key roles on the journey for commercially attractive MFC production. Adequacy of a rather heterogeneous MFC with dimensions at the upper end of the nanoscale offer remedy on this course.

The question of pre-treatments still hangs over the issue. Enormous energy savings have been proven and even higher ones hypothesized with the utilization of enzymes or chemicals. Chemical treatment could introduce other desired properties as well, as some derivatised fibrils give better strength properties with less dewatering problems than their non-derivatised rivals. It is outside the scope of this thesis to determine whether an enzymatic or a chemical pre-treatment would be worth the price of the agent, a more complicated process layout with washing and possible chemical recovery, longer payback period, possible complications at the wet end, and establishing a steady supply for the pre-treatment agent. One thing seems certain - without one, multiple passes through the refiner, or several refiners in series, is a requirement for the desired degree of fibrillation and uniformity of the product. It is a challenge, but not a roadblock.

The effects of hornification on MFC production raise dispute. Majority of the literature indicate slightly harder fibrillation meaning more energy is required to produce MFC with similar bonding ability and strength enhancement as with neverdried pulp. The reported differences are often small and some studies report no difficulties at all with dried fibres. The controversy in the results can indicate that the effects of hornification are small and random deviation in results can swing the conclusions to either side. On nanoscale, sufficient evidence exists for the theory that hornification leads to larger microfibril aggregates. It might be that the effects of hornification manifest only when the fibrillation

is extended to the smallest particle size possible. In that case, hornification should not prove to be a problem with the targets set for this work.

It is evident from the literature, that MFC is too complicated and diverse a material to be characterized comprehensively by any single method. Furthermore, the most comprehensive characterization techniques often require extensive preparations and prolonged time. Thus, they are not realistic in a mill environment. A sufficient, indicative online characterization method is needed. Various optical measurements are probably sufficient, as they can yield information on fibre dimensions, degree of fibrillation, and homogeneity. Viscosity might be a good candidate as well. Combined with the refiner energy consumption and perhaps an ionic strength measurement should generate enough information for controlled, continuous production of MFC. Another approach would be screening the MFC. If sufficient degree of fibrillation and homogeneity is guaranteed by efficient screening, characterization can be done by more cursory methods. Successful implementation of MFC production on-site requires that a connection between the various measurements and the impact on paper mechanical and optical properties is established and well understood.

There is hardly a more complicated area at a paper mill than the wet end. Bringing microfibrillated cellulose in that kettle of fish requires steady nerves and profound knowledge. MFC fiddles seriously with the holy trinity of papermakers - water removal, formation, and retention. MFC with its enormous surface area and armada of free hanging hydrogen groups, longing for bonding, is kryptonite for water removal. Yet, as has been shown, careful optimisation of the wet end chemistry, with the little help from cationic polyelectrolytes, can revoke this headache. That is especially true if the filler content of the furnish can be increased. Optimisation is required for the controlling of formation as well. To distribute MFC evenly in the stock, efficient mixing is needed. Still, MFC reportedly improves formation. This is probably due to the short length of microfibril aggregates, as refining has the same effect on formation owing to the reduced fibre length. Retention of MFC and its contribution to the retention of other substances is another thing and depends on the whole of wet-end chemistry.

Even though this thesis focuses on papermaking, a cost-effective production method for MFC could open opportunities in other applications as well. For pharmaceuticals or other high-end applications, the acquired product could be too heterogeneous. However, as rheology modifiers in oil industry, paints, cements, food industry, and cosmetics, the properties likely meet the requirements. Composites offer another field for potential applications. The challenge is to fit the production scale to each application, or to achieve MFC that can be dried for transport and redispersed.

Finally, a subject not extensively covered in this literature review but worth mentioning altogether, is whether production of MFC could be used at a paper mill to control external and internal fibrillation separately. If the pulp refiners were more tuned towards internal fibrillation, MFC could take up the role of the external fibrillation. This would allow the control of refining in a whole new level compared to present situation. How remarkable a change the separate control of internal and external fibrillation would be, and what grades would benefit most from it, is a question for another thesis. Also, paper industry is not famous for its pioneering spirit. New technologies tend to be embraced only after extensive piloting or someone else doing it first. This is unsurprising given the scale of modern paper and board machines, and the price it takes to halt production even for short periods. Perhaps one day some small specialty paper manufacturer becomes the trailblazer on this practice.

7. Experimental part

The target of the experimental part is to confirm the findings of the literature review in practice and to test the effects of certain refining parameters, like intensity and consistency, on MFC refining and the end-product. Experimental part covers laboratory work, pilot runs, and characterization of the samples. The main sections are preliminary experiments, primary experiments, characterization, and conclusions. Standard characterization and preparation methods used in this work are listed in Table 3.

Experimental designs considering the primary trials are in the appendices. Original experimental design (Appendix B) was refined (Appendix C) after challenges in the primary trials. Experimental designs are written in Finnish. In the original experimental design, three main variables were set for inspection: edge load, consistency, and flow speed. For load and consistency, maximum values were to be determined and compared to lower values. Also, starting with high load or consistency and decreasing that value during refining was to be experimented. For flow speed, two values with constant load and consistency were set for testing.

Table 3. Standards and methods.

Pulp characterization	**Standard**
Schopper-Riegler	ISO 5267-1
Viscosity (cup and bob measuring gap adjusting)	ISO 3219 & DIN 53019-1
Laboratory sheet preparation	**Standard**
Laboratory sheet preparation	ISO 5269-1
Hot disintegration of TMP	ISO 5263-3
Laboratory sheet characterization	**Standard**
Sheet thickness	ISO 534
Optical measurements: ISO brightness, whiteness, opacity	ISO 2470 & ISO 5631
Tensile test	ISO 1924-3
Internal bond strength	TAPPI T 833 pm-94
Other methods: Valmet Fiber Image Analyzer FS5, Valmet Pulp Analyzer MAP, Light microscope, SEM Phenom Pure	

7.1 Materials and methods

Majority of the experiments were run at Åbo Akademi's Laboratory of Fibre and Cellulose Technology in Turku in southern Finland using the Laboratory's Metso ProLab™ LC refiner with various refiner fillings. Laboratory sheets for mechanical tests were prepared at Åbo Akademi and at Aalto University's Department of Bioproducts and Biosystems in Espoo in southern Finland. MFC films were prepared at Aalto University.

Pilot runs with an industrial scale refiner were done at Valmet R&D centre at Inkeroinen in south-eastern Finland. Two different set of fillings were used with similar refining sequence as was used with ProLab™.

Characterization was done by several means. Most important methods were tensile tester, internal bond tester, optical fibre analysis, and freeness measurements with a Schopper-Riegler device.

7.1.1 Materials

Bleached birch kraft pulp was acquired from a Finnish pulp mill. Neverdried and dried pulp were supplied from the same batch. Pulp was diluted to target consistency and slushed before letting into the mixer. In the case of low consistency neverdried pulps, slushing was replaced by mixing with a hand-held cement mixer. A thorough description of the refining sequence is given in the section *7.1.2 ProLabTM.*

For internal bond strength measurements, spruce TMP from a Finnish magazine paper mill was used. A standard hot disintegration treatment was given to the frozen TMP. Cationic starch was kindly provided by Chemigate Oy.

7.1.2 ProLab™

Adapted from Erik Sjöström's work

ProLab™ is used to research the effects of refining on fibres in conditions similar to those in the industry. ProLab™ is a batch type refiner operating in low consistency. Batch size is 35-60 litres. The equipment consists of a pulper, a mixer, a stock feed pump, a refiner,

and a sampling section with six automatic valves delivering pulp at pre-selected SEC values (Figure 14). More samples can be acquired by manual operation of the sample valves.

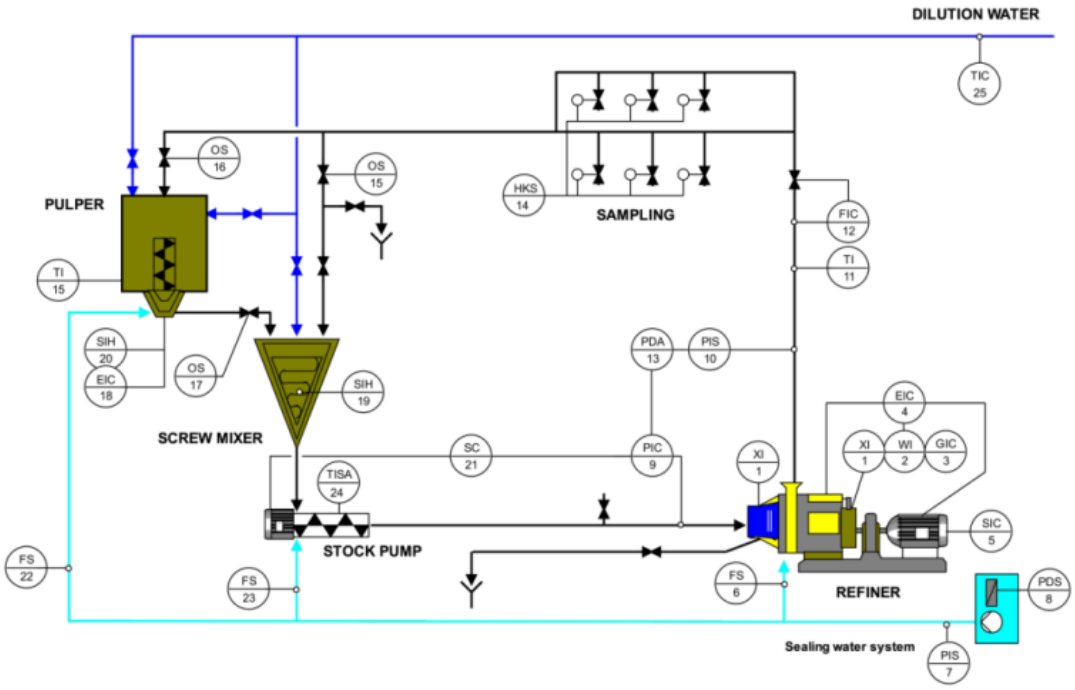

Figure 14. ProLab™ schematics (Lundin 2008).

Idle power consumption is determined for each filling separately as explained in the chapter *4.2.2 Theories on refining*. Energy efficiency is monitored by tracking refiner total energy consumption and specific energy consumption. Pumping, mixing, and other energy consumption sources were not included in these calculations.

Bar clearance is monitored by a linear position sensor from the rotor axial motor. The physical touchpoint of the fillings is determined by a zeroing process and stored as a specific vibration level to avoid collision during refining. The vibration sensor is attached to the stator. Vibration decreases as the pulp gets more refined, allowing smaller gap clearance over time.

ProLab™ controls include gap clearance, rotor rotating speed, and pumping intensity or flow speed. Automatic or manual controls can be used. Automatic power control targets a

specific refiner load and adjusts the gap accordingly. Manual controlling is done by adjusting the gap clearance or refiner load.

New fillings are given a sanding procedure to make them match each other better and wear out the fillings corresponding better to refining conditions in the industry.

Figure 15. ProLab™ laboratory refiner.

7.1.3 Film casting

MFC films were cast in a custom pressure chamber device with a 1.5-2.5 bar pressure using a 10 µm polymer filter. Cast films were dried between pressurized hot plates at 80 °C temperature. They were then further dried in a 103 °C oven until weight remained stable, weighed for grammage, and conditioned in standard conditions for at least 24 hours before mechanical and optical measurements.

7.1.4 Characterization

Primary characterization device was a tensile tester. Laboratory sheets with varying MFC contents from different trial runs were prepared and characterized. In the preliminary experiments, highly refined pulp was mixed with unrefined pulp of the same origin. In the

primary experiments, a pre-refined pulp with SR 35 was prepared as a stock pulp to correspond better with industrial conditions. Tensile tests were also done for MFC films and TMP sheets with varying MFC content. The principal purpose of TMP sheets was to evaluate the usefulness of MFC in a multilayer board, such as liquid packaging board. Thus, internal bond strength of TMP sheets with and without MFC was measured.

Pulp freeness was measured by a Schopper-Riegler device. Dry matter content was measured by weighing samples before and after drying in a 103 ^{o}C oven until weight remained stable.

Brightness, opacity, and ISO whiteness were measured for MFC films. Light microscopy images were used to evaluate visually the heterogeneity of fibre length and length reduction development during refining. SEM images from MFC films and freeze-dried MFC samples were also taken.

Selected samples were sent to Valmet Technology Center in Kajaani for detailed fibre analysis. Methods used included Valmet Fiber Image Analyzer FS5 and Valmet Pulp Analyzer MAP.

7.1.5 Rheometry

Rheological measurements were performed in 3 % consistency. Samples were prepared by diluting MFC samples into 100 ml batches and left to warm up close to room temperature before testing. Tests were done on a Physica MCR 300 Modular compact rheometer in the Laboratory of Paper Coating and Converting, Åbo Akademi. Concentric cylinder measuring head CC 27 was used. Tests were run at 25 ^{o}C temperature first with an oscillation measurement frequency sweep from 0.1 to 100 Hz at fixed amplitude of 1 %. Then, after a 60 second pause to ensure sample stabilization, a shear stress test with shear rate sweep from 0.1 to 1000 s^{-1} was run.

7.1.6 Preliminary experiments

Preliminary experiments were done for several reasons. Firstly, to explore the equipment and discover its strengths and limitations. Secondly, to get indicative results whether the equipment was able to refine pulp far enough for it to be considered MFC. Lastly, the role of hornification was evaluated by comparing neverdried and dried pulp refined to same SEC.

To test ProLab^{TM}'s suitability for MFC production, modified SF fillings were used (Figure 16). More important than characterizing the end-product as MFC was its strength enhancement potential in paper. Thus, hand sheets with 20 % load of achieved pulp products were made and compared to a control sample by a tensile tester. Pulp samples were measured for Schopper-Riegler (SR) during the refining. Samples were also evaluated by Kajaani FibreLab analyser, light microscopy, WRV, and mechanical and optical tests for cast films.

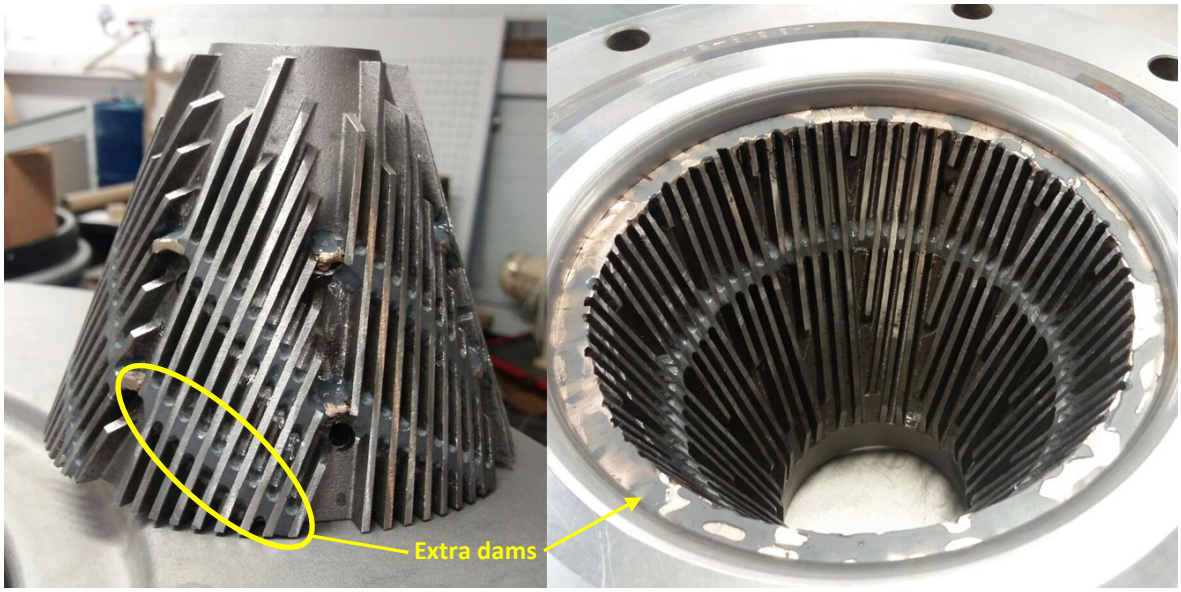

Figure 16. Modified SF fillings.

7.2 Results

Preliminary experiments with modified SF fillings were promising yielding fair results and indicating a right track for further experiments. For the primary experiments, customised Lab-13 fillings were manufactured. Due to complications with these fillings, most of the main experiments were carried out with the modified SF-fillings.

Statistical significance was evaluated by analysis of variance in case of groups and by Student's t-test when comparing two test points where statistical analysis was needed.

7.2.1 Preliminary experiments

In the preliminary experiments, a highly refined pulp with properties close to MFC was obtained when the pulp was refined to SEC 1 200 kWh/t. Pulp had rigid structure and film casting produced opaque films rather than paper (Figure 17). At around SEC 700 kWh/t, the SR value of the pulp rose above 90 which is close to the upper limit of measurement with the device.

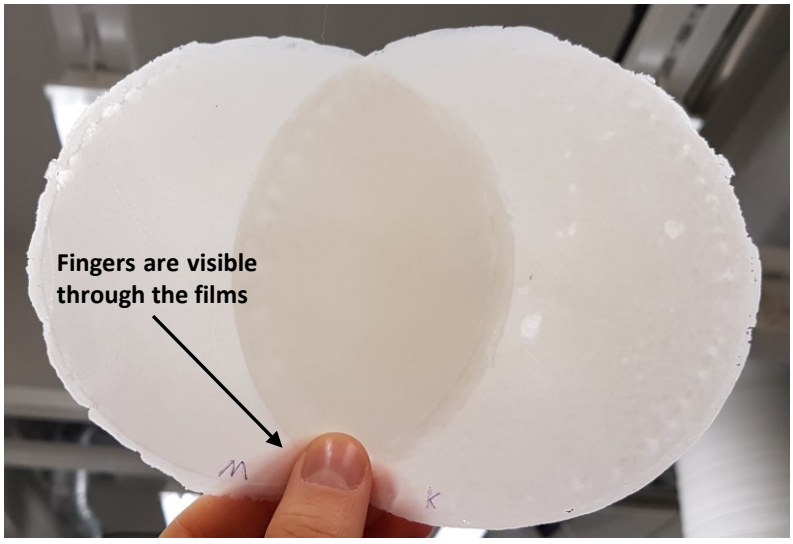

Figure 17. 42 g/m2 films from highly refined neverdried (left) and dried (right) pulp.

Coefficient of efficiency, the ratio of net power to total power intake, of the refiner was 45 % for neverdried and 44 % for dried pulp resulting in a total energy consumption of around 2 700 kWh/t. SR values at SEC 500 kWh/t for neverdried and dried pulp were 80

and 82, respectively. Since the process and characterization involve some variables even with automation and same settings, such small differences are neglectable. However, a difference in fibre average length was observed as shown in Table 4. Hornified fibres were cut more profoundly than neverdried fibres at the beginning of refining, which corresponds to literature. Most notable difference was observed at SEC 1 000 kWh/t. As refining continued, the difference grew smaller. Probably the fillings used do not easily cut fibres below the length of 0.3 mm. SF fillings in question have 2 mm bar width, 2.5 mm bar distance, and cutting length of 249 m/rev.

Table 4. Fibre average length in preliminary experiments.

Fibre average length [mm]	SEC 500 kWh/t	SEC 1 000 kWh/t	SEC 1 200 kWh/t
Neverdried	0.67	0.39	0.32
Dried	0.61	0.31	0.29

Mechanical and optical properties were evaluated with 42 g/m^2 and 69 g/m^2 cast films (Table 5). Despite the difference in fibre length, mechanical properties were similar and variation within samples exceeded variation between films made of either neverdried or dried pulp. Neverdried pulp produced whiter and brighter films. Same phenomenon was observed with naked eye – dried pulp was slightly yellow of colour whereas neverdried seemed pure white. However, such small differences should be of no concern with the percentage of MFC that is sensible in paper applications. Thus, it seemed that neverdried and dried pulp are both equally suitable for MFC-like, highly refined pulp production. As was concluded in the literature review, the role of hornification in MFC production might only manifest when fibre dimensions approach nanoscale.

Table 5. 42 g/m² MFC-film mechanical properties.

Film properties	Neverdried	Once-dried
Tensile strength index [Nm/g]	74 ± 4	71 ± 5
Stretch [%]	1.6 ± 0.3	1.6 ± 0.3
Stiffness index [kNm/g]	9.0 ± 0.3	8.8 ± 0.3
Whiteness	109	82
ISO Brightness [%]	85	76
Opacity [%]	38	40

Strength enhancement potential with the highly refined pulp was evaluated by doing tensile tests with hand sheets of unrefined pulp with 20 w-% load of SEC 500 kWh/t and SEC 1200 kWh/t refined pulp, and comparing the results to reference sheets with 100 % unrefined pulp. As was expected, the tensile strength index (TSI) increased significantly with the addition of highly refined pulp (Figure 18). These preliminary tests were of limited scope and further conclusions should be drawn carefully. However, the tests indicate that desired properties are achieved at relatively low refining values and further refining seems to provide little enhancement compared to the energy consumption.

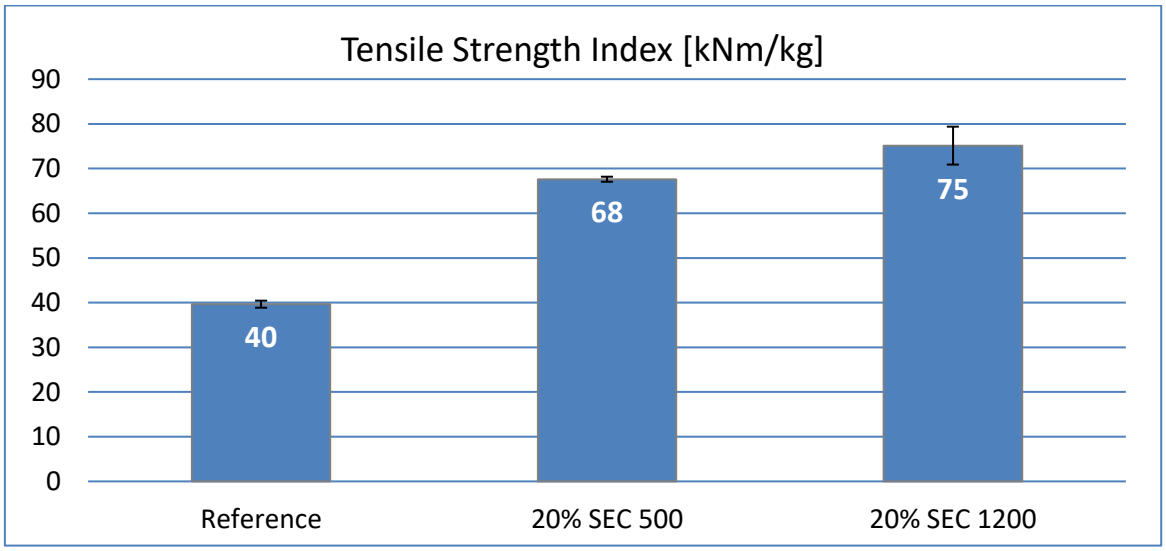

Figure 18. Increase in tensile strength with 20 % addition of highly refined pulp.

7.2.2 ProLab™ trials with original experimental design

The primary experiments were done to evaluate the effects of different refining parameters, mainly intensity and consistency, on refining and the end-product. The experiments with ProLab™ were started with Lab-13 fillings (Figure 19). Several complications with the fillings arose. First, it was hard to load the fillings even close to values obtained with SF fillings due to frequent collisions. The stator and rotor were not aligned precisely causing the fillings to touch on one side of the stator before proper edge load was reached. Several sanding procedures were performed in order to better align the fillings. During these procedures, the groove depth was diminished to less than half of the original from one side of the stator to little avail. This led to prolonged refining times with poor energy efficiency, overall difficulties in process control, and probably more heterogeneous refining as fibres could pass through the refiner either virtually unprocessed on one side of the stator or under severe load on the other side.

Figure 19 depicts another challenge with Lab-13; clogging of grooves. Both rotor and stator had to be scraped free of trapped fibre bundles after each trial. Clogging was logically most severe against dams, though smaller amounts of fibre bundles were trapped everywhere along the grooves. Shortening and softening the fibres by a pre-refining treatment with regular SM short fibre fillings was tried out. Pre-refining was run to SEC 500 kWh/t. The length-weighted fibre length decreased from 1 mm to 0.4 mm and SR value increased from 12 to 86. With the pre-refined pulp, process control with Lab-13 fillings proved even more troublesome than with unrefined pulp. Fillings touched each other at very low edge load leading to coefficient of efficiency of below 10 % after several hours of refining. At that point, SEC value was increased by 100 kWh/t to a total of 600 kWh/t. No noticeable difference in SR value or fibre length compared to the pre-refined pulp was observed.

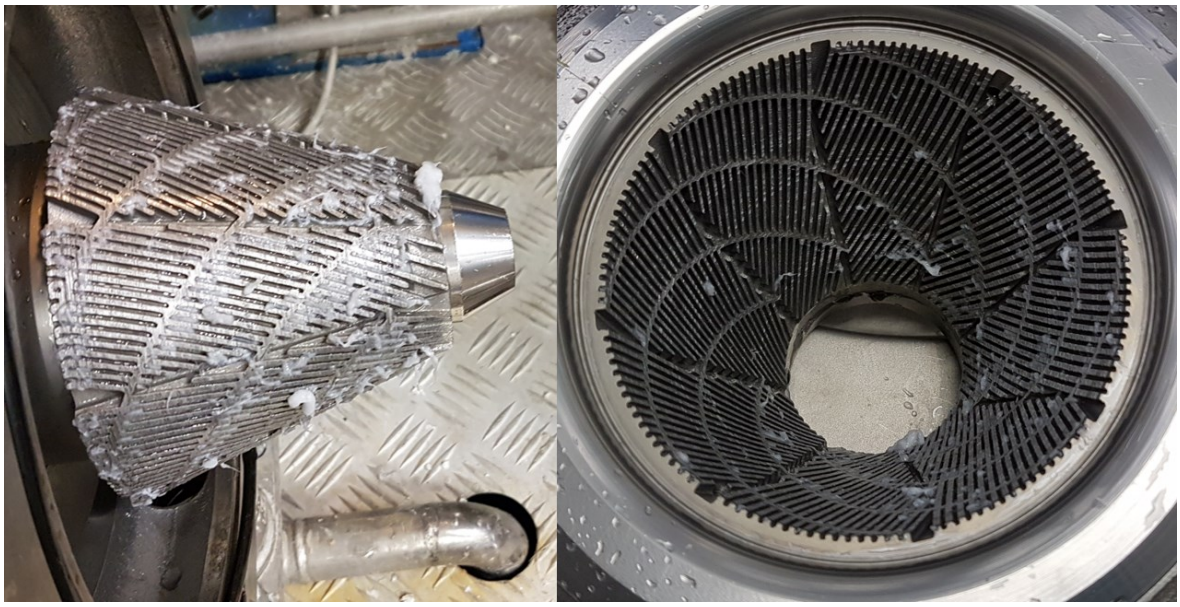

Figure 19. Lab-13 fillings for ProLab™ with grooves filled with pulp after a trial.

The material, 3D-printed aluminium, caused challenges too. Figure 20 illustrates how the relatively soft aluminium bars became burred, and at some parts, blocked the grooves in the course of several trials and sanding procedures. Also, fibre shortening was less pronounced with the Lab-13 fillings than the SF fillings. It is also possible that the softer aluminium bars cause less severe impacts on fibres than steel bars would. Peculiar spuns of fibres were observed attached to the grooves after trials and it was concluded that this was caused by the burring of the bars and weaker fibre length reduction. Such objects would be detrimental to paper properties. This phenomenon was not observed in any other experiment with the other fillings.

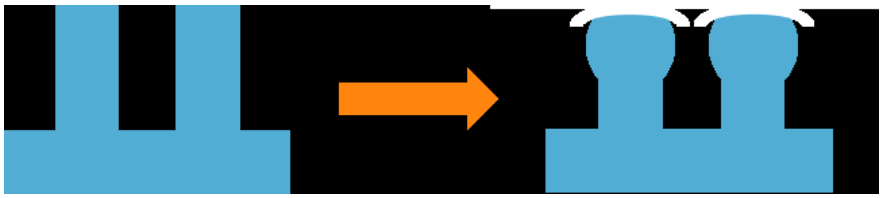

Figure 20. Simplification of the wear of aluminium fillings.

Definite conclusions whether the Lab-13 dimensions, bar width of 1.0-1.2 mm, groove width of 1.6-1.8 mm, and groove depth of 2.0-3.5 mm, are suitable for MFC refining or not, cannot be deducted from the trials since majority of the challenges were related to

poor alignment and material. Still, there is clearly room for product development. In a patent by Heiskanen et al. (2016), MFC refiners were indeed described as having a groove depth of around 2-3 mm, as was the case with Lab-13. However, no reference value for the narrowness of grooves for MFC-refining was found. Since SF fillings proved effective with considerably larger bars and cutting length of 249 m/rev compared to 900 m/rev of Lab-13, Lab-13 bar dimensions might be simply too small. Also, Lab-13 might have been too heavily dammed.

Though actual MFC or product close to that was not achieved with Lab-13 fillings, some questions in the experimental design were answered. Due to limitations in ProLab™ programming, flow speed could not be altered in a controlled and reliable way. A flow speed of around 50 l/min was used in all trials. Also, it was found in the preliminary trials and trials with Lab-13 fillings that operating at a pre-determined path for decreasing load by force was not reasonable, since it leads to collisions of fillings and moments of unnecessarily low load. Instead, using either maximum load possible at any given moment or a constant, low load was deemed worth testing. Additionally, a pre-set path for decreasing consistency whilst starting at 5-6 % DMC was found to be unnecessary. Instead, basing decisions on consistency reductions on the development of pressure and temperature was deemed reasonable. It should be noted that these conclusions were based on a batch-type laboratory refiner. In a continuous, industrial plant optimized, pre-determined values for edge load and consistency on every refining step as well as adjusting those variables on the run based on refining parameters is essential.

7.2.3 ProLab™ trials with revised experimental design

The revised experimental design continued where previous part ended, evaluating the effects of different refining parameters. Four trials answering to the role of edge load and consistency were executed. MFC samples were labelled according to refining parameters as shown in Table 6. Here high consistency refers to the upper end of LC refining and was 6.1 % for HCHL and 5.5 % for HCLL. However, as the refining proceeded beyond SEC 500 kWh/t with HCHL, the pulp had to be diluted to prevent overheating and overpressure in the equipment due to growing viscosity. Samples were taken for DMC measurements

after every dilution to calculate actual SEC values. High load refers to refining done with maximum load that the equipment was capable of handling without overheating, overpressure, or collision of fillings. In the beginning, maximum load was limited by the pressure difference before and after refiner. As the refining advanced, fillings started to touch each other and load had to be gradually decreased to prevent collision. At around SEC 1 500-2 000, temperature approached ProLab^{TM} safe limit of 80 ^{o}C. In the case of HCHL, a one-hour pause was held before continuing to the end.

Table 6. MFC classification according to refining parameters.

Sample ID	Definition	Consistency	Refiner median net load SEC 0-500	Refining end point (SEC)
HCHL	High consistency, high load	6.1->4.1%	8.6 kW	2 500
LCHL	Low consistency, high load	3.5%	10.3 kW	2 000
HCLL	High consistency, low load	5.5%	2.5 kW	500
LCLL	Low consistency, low load	3.5%	2.5 kW	500

In theory, higher consistency should enable higher refiner load as there are more fibres sharing the load and preventing fillings collision. With more robust equipment, maximum refiner load would have probably been higher for HCHL than for LCHL.

7.2.4 Pilot trials

The target of the pilot trials was to replicate the results of laboratory trials in a commercial scale. Pilot runs were conducted in Valmet R&D centre in Inkeroinen. Refining was carried out with an industrial scale JC-01 conical refiner with two set of fillings: PSED, a decade old design for short fibre refining with additional dams, and a modern Microbar design (Figure 21). Dried Finnish birch kraft pulp from different mill than the one used in laboratory trials was used. SR value of the pulp in pilot trials was 14 and 12 for the one used in laboratory runs.

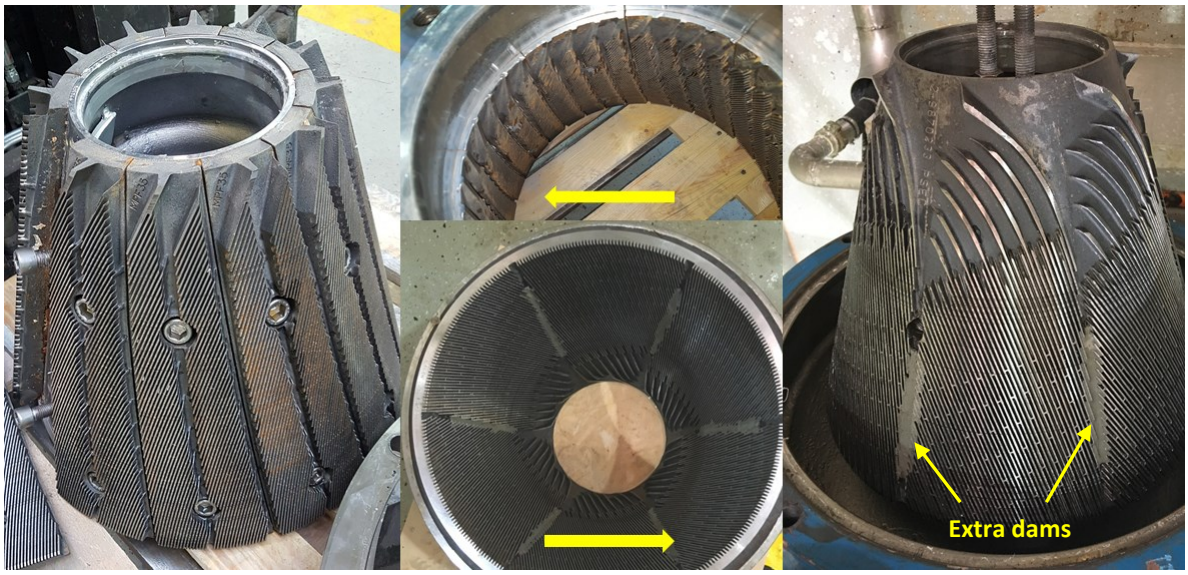

Figure 21. Microbar (left) and PSED (right) refiner fillings.

Pulp was circulated for 24 passes through the refiners in both runs. Microbar allowed higher load leading to SEC 850 kWh/t. With PSED, SEC 750 kWh/t was reached. After five passes, SEC was already close to 500 kWh/t. In both runs, load had to be reduced profoundly at around SEC 200-400 as can be seen in Figure 22. Similar phenomenon was observed in laboratory runs, though not as strongly and early on the SEC curve. It should be noted that each filling had different bar configuration which affects edge load and loadability.

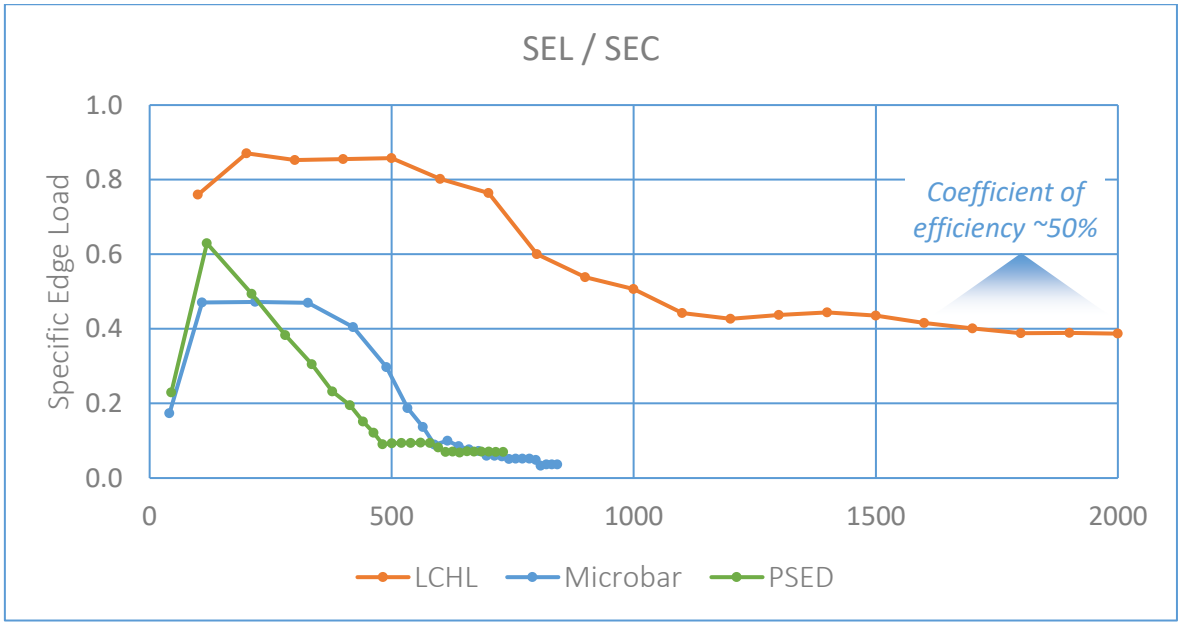

Figure 22. Development of SEL in pilot runs with ProLab™ LCHL as a reference.

Fibre analysis with FS5 further confirmed the precedence of Microbar over PSED as can be seen in Table 7. Microbar caused better fibrillation, reduced fibre dimensions more extensively and produced higher number of fines than PSED. Descriptions of the FS5 parameters can be found in Appendix A. Ten years of product development is evident in the results. As the better performing option of the two, Microbar was chosen for comparison between laboratory scale and pilot scale experiments. In other graphs, "Pilot" refers to Microbar-refined pulp.

Table 7. Fibre analysis of Microbar and PSED refined pulps.

Fibre analysis after 24 passes	**Microbar**	**PSED**
Share of fibre length fraction 0.0-0.2 mm	86 %	77 %
Fibre length Lc(l) mm	0.099	0.144
Fines-%	74 %	59 %
Fibrillation-%	0.96 %	0.74 %

Comparison between the fibre properties of laboratory and pilot trials at SEC 500 are presented in Table 8. LCHL was chosen for the comparison as it performed best in the laboratory trials. It should be noted that LCHL was refined in 3.5 % consistency and pilot run with a pulp of 4.0 % consistency. This should nudge the results slightly in the favour of LCHL. Still, pilot runs indicate higher degree of refining and fibrillation in all fibre characteristics. If the target is in highly refined pulp instead of proper MFC, pilot trials were very promising. Further fillings optimization for MFC production should yield additional improvement. How to refine the pulp further from the point when proper edge load is lost is a key question if actual MFC is to be produced. Probably there is something in the scale or geometry of ProLab^{TM} refiner that enables efficient refining for prolonged periods. Even at SEC 2 000 kWh/t, efficiency of LCHL refining was around 50 %, while with Microbar the efficiency dropped to around 15 % at SEC 800 kWh/t (Figure 22). With larger refiners, the extremely small blade gap needed seems to be more difficult to control. This is illustrated in Figure 23. Though the gap values between laboratory and pilot trials might not be exact and directly comparable, it is easy to see how problematic maintaining as small gap as possible with JC-01 was compared to ProLab^{TM}. Figure 23 also clearly

illustrates the difference consistency makes for bar clearance. HCLL and LCLL are kept in constant load and the gap clearance is almost double for 5.5 % than for 3.5 % consistency.

Table 8. Fibre analysis comparison between pilot and laboratory trials at SEC 500 kWh/t.

Fibre analysis at SEC 500 kWh/t	**Pilot (Microbar)**	**Laboratory (LCHL)**
Share of fibre length fraction 0.0-0.2 mm	80 %	72 %
Fibre length Lc(n) µm	41	51
Fines-%	59 %	50 %
Fibrillation-%	0.75 %	0.59 %
Schopper-Riegler value	93	88

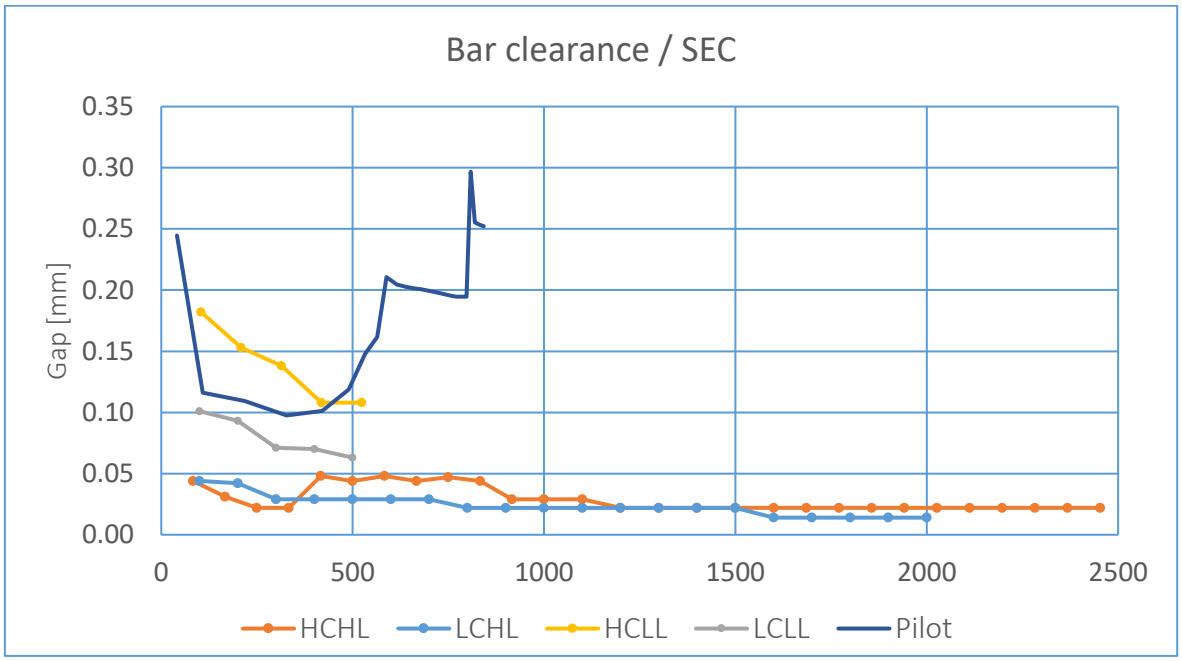

Figure 23. Bar clearance between different laboratory runs and pilot run with Microbar fillings.

7.2.5 Fibre analysis – comparison of different refining methods

Table 9 lists fibre analysis results for SEC 500 kWh/t pulps obtained by Valmet Fibre Image Analyzer FS5. Pulp pre-refined to SR 35 is used as reference. Figure 24 illustrates the results of Table 9. Fibre properties are scaled by highest value in each category. Fibre length and width are turned the other way around; higher percentage stands for shorter and narrower fibres. Fibre width measurement with pre-refined pulp contains some sort of error and is marked with red.

Table 9. Fibre characteristics measured by FS5 for SEC 500 kWh/t pulps.

Sample ID	Length Lc(n) µm	Fibre width µm	Fines A %	Fibrillation-%
Pre-refined	73	13.6	20 %	0.26 %
Pilot	41	19.9	59 %	0.75 %
LCHL	51	17.6	50 %	0.59 %
HCHL	57	18.4	41 %	0.46 %
HCLL	62	17.5	38 %	0.42 %
LCLL	62	16.8	38 %	0.42 %

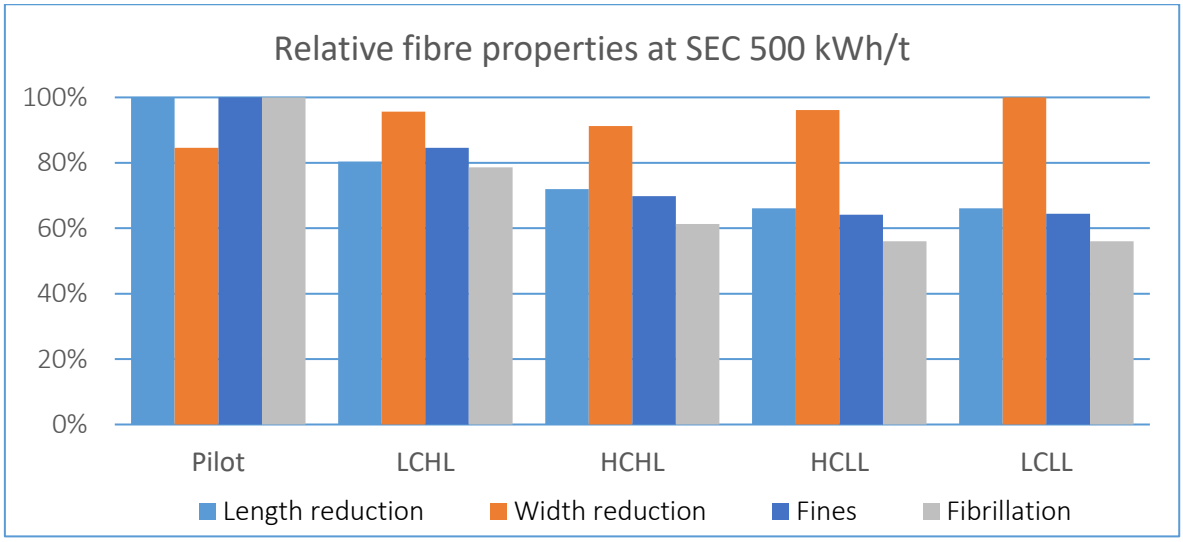

Figure 24. Relative fibre properties scaled by pilot trial.

Clear trend is evident in fibre length, share of fines, and fibrillation. Pilot trial performed best in all three, then low consistency high load laboratory run. Last ones were trials done with low edge load. Interestingly, fibre width did not follow the same pattern. Though the differences were not as outstanding as with the other three properties, low load seems to reduce more width compared to length than high load. Using length-weighted fibre length, the aspect ratio for Pilot, LCHL, and LCLL is 7, 11, and 18, respectively. High aspect ratio gives structural strength of the fibre backbone in addition to added hydrogen bonding and should therefore lead to higher strength enhancement. On the other hand, MFC is highly hygroscopic material and longer fibrils might lead to loss in dimensional stability and tension in the paper matrix. However, optical fibre measurement is accurate

only above dimensions of 0.2 µm and the aspect ratio of fibrils cannot be concluded from that of fibres.

Values for external fibrillation are notably low. Fibrillation values measured right after refining at Inkeroinen were three times higher than the figures shown here that were measured few weeks later at Kajaani. Loss in fibrillation might be caused by imaging settings, since external fibrils might not be classified as such once they have time to swell. Another reason would be that fibrils tend to attach to the fibre surface and to each other during storage. This would mean that MFC starts to lose its functionality in a relatively short period. A thorough assessment of MFC's properties over time would be needed to assess this phenomenon. No such loss in Fines A % was observed.

Figure 25 gathers light microscope images of the SEC 500 kWh/t samples. Further fibre length analysis is provided by the length fractions in Figure 26. Microscopy confirms the quantitative fibre data; pilot trial produced more homogeneous product and generally smaller fibres than laboratory runs. Every ProLab™ sample contains significant amount of larger fibres or fibre particles making the product highly heterogeneous. This was further confirmed with SEM imaging as shown later (Figure 34).

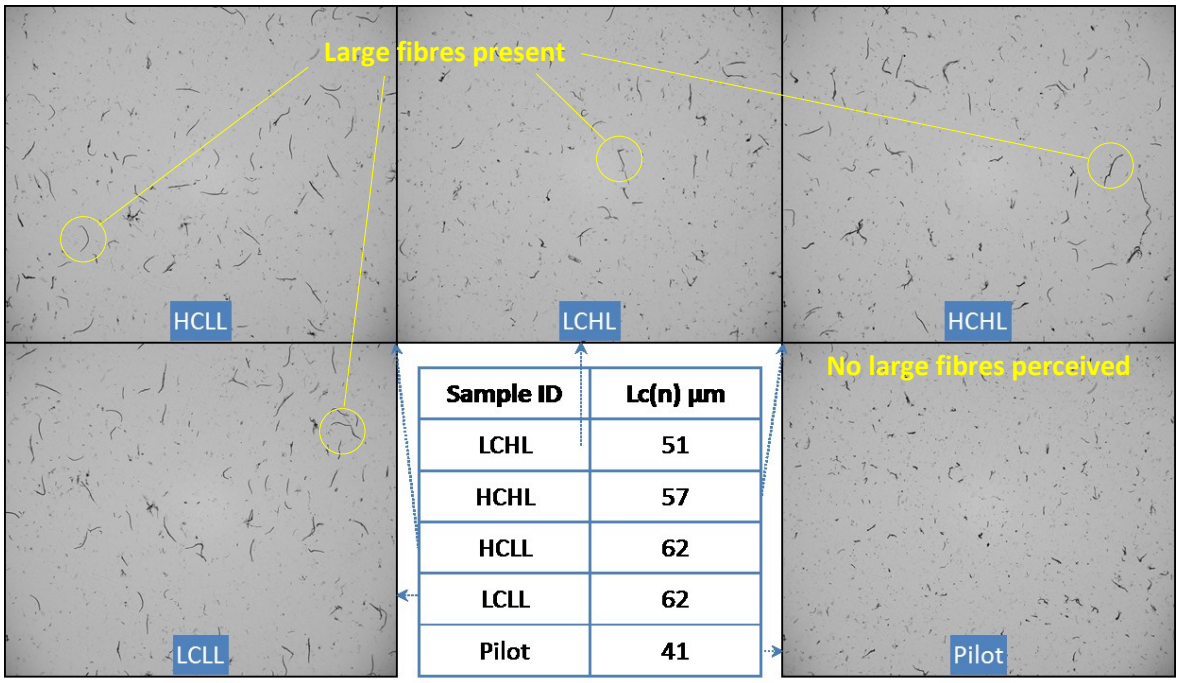

Figure 25. Light microscope images of SEC 500 kWh/t samples obtained by a FS5 analyser.

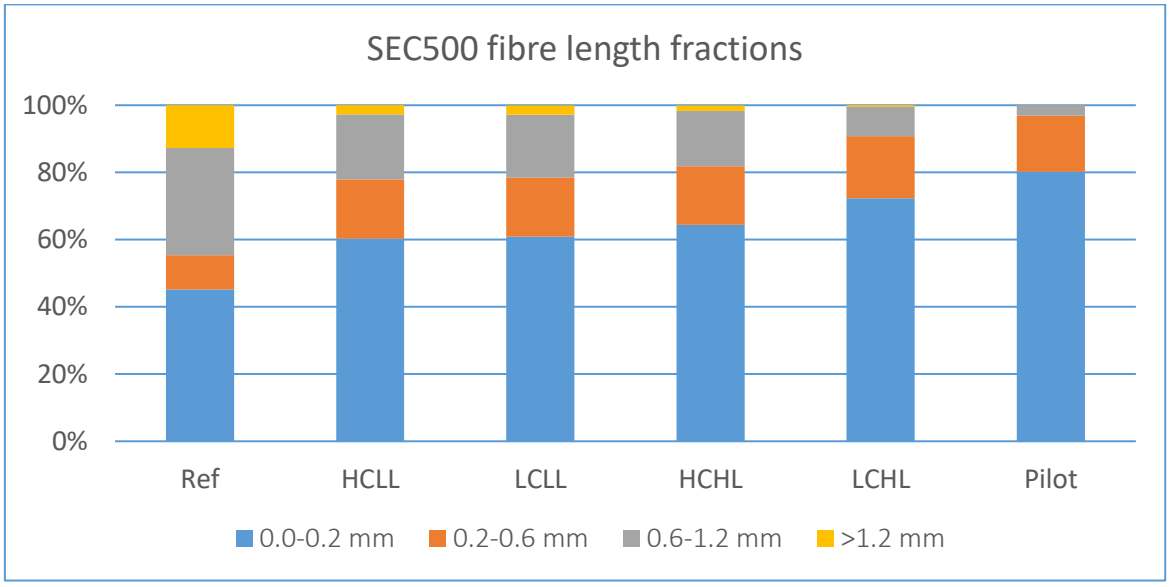

Figure 26. Fibre fractions of SEC 500 kWh/t samples measured by FS5 analyser.

Schopper-Riegler measurements gave similar results as fibre analysis (Figure 27). Increase in SR correlates with the amount of free hydrogen groups and potential strength enhancement and is thus desired. In the beginning of refining, SR value rose sharply from SR 12 of unrefined pulp to around SR 80-90 at SEC 500 kWh/t. The value rose most

sharply in the pilot trial and was lowest for HCLL, though differences between laboratory runs are small.

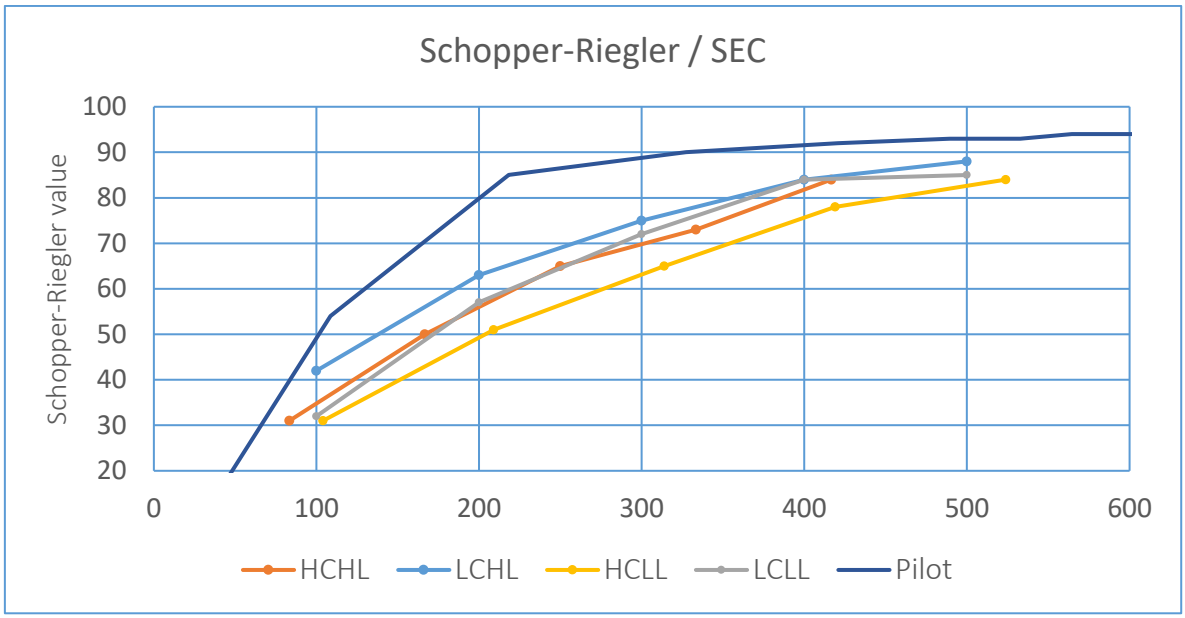

Figure 27. Schopper-Riegler development during first 500 kWh/t SEC.

Both automated fibre analysis and freeness measurements seem to be good indicators of degree of refining. However, freeness should only be used in the beginning since it quickly loses its accuracy when the share of fines and fibrils passing through the wire increases. Most comprehensive understanding of the product is achieved by combination of several parameters as can be seen when fibre width is compared to other properties. As was stated in the literature, higher refiner load and lower consistency lead to more fibre cutting. Fibre length reduction is a two-sided issue as some reduction is inevitable and desired. On the other hand, high aspect ratio could give better strength enhancement. Still, length reduction from 73 µm of the pre-refined pulp to 41 µm of pilot trial does not sound too severe. Length reduction of only 15 % for HCLL and LCLL is quite remarkable as at the same time fines-% and degree of external fibrillation almost doubled from that of the pre-refined pulp. It should be noted that HCLL and LCLL did not start with pre-refined pulp, but received their gentler treatment from the beginning. Pre-refined pulp was refined to around SEC 100 kWh/t with much higher load using the same SF-fillings. Thus, more comprehensive analysis for this specific phenomenon is needed if high aspect ratio

is targeted. Overall, produced material is very heterogeneous as was expectable according to the literature.

7.2.6 Fibre analysis – development over SEC

Development of fibre properties over prolonged refining is shown in Table 10 and illustrated in relative values in Figure 28. Figure 29 illustrates the effects of refining and fibre length reduction with light microscope images, and Figure 30 gives insight in the fibre fractions development. LCHL was chosen for detailed examination as it was the best performing refining method in laboratory trials.

Table 10. Development of fibre properties with LCHL.

SEC kWh/t	Length Lc(n) µm	Fibre width µm	Fines A %	Fibrillation-%
100	73	13.6	20 %	0.26 %
500	51	17.6	50 %	0.59 %
1000	41	5.8	72 %	1.08 %
1500	38	4.9	84 %	1.27 %
2000	36	4.5	90 %	3.18 %

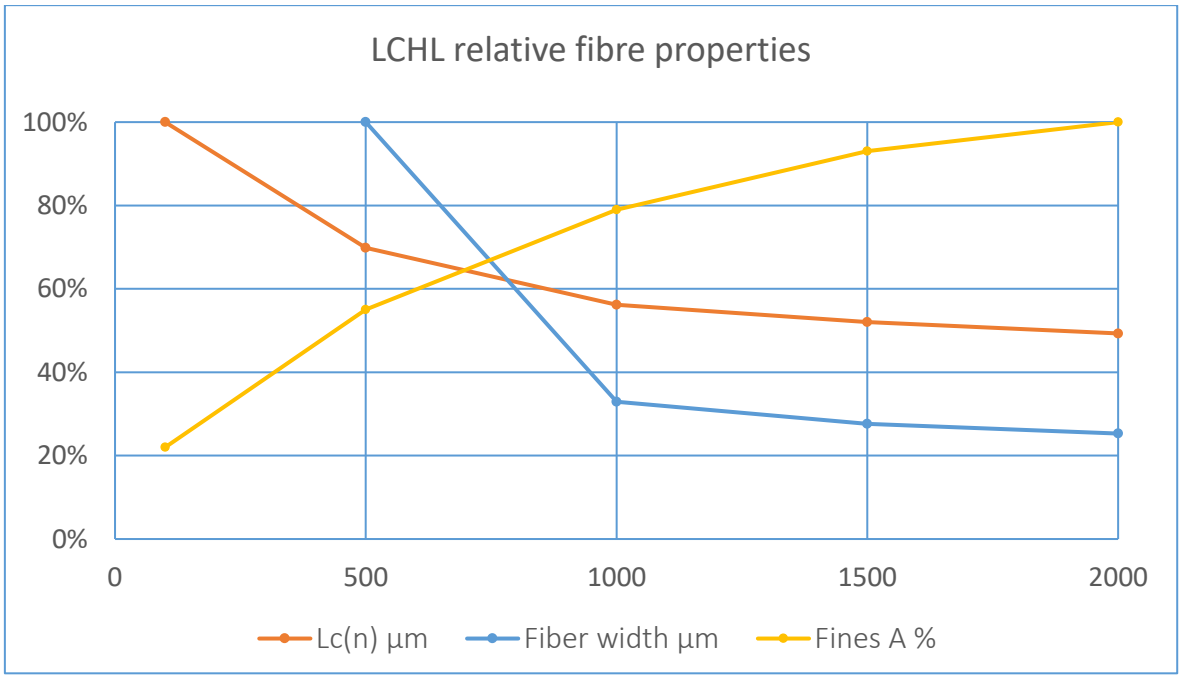

Figure 28. LCHL relative fibre properties over SEC.

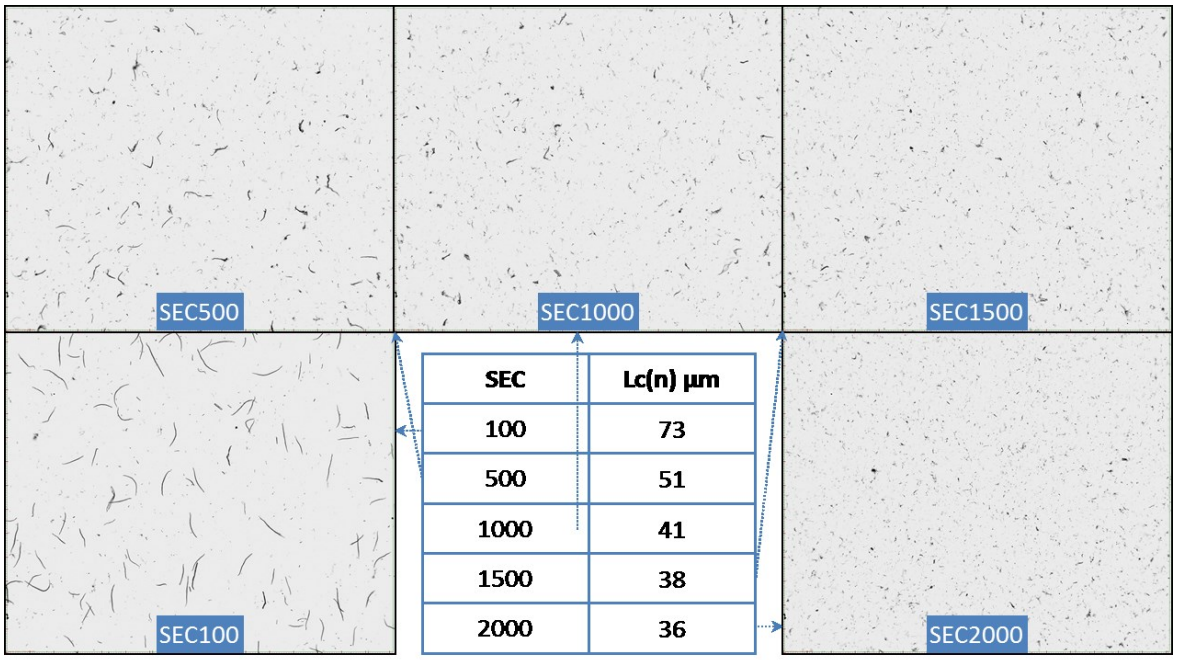

Figure 29. Light microscope images of LCHL refined to different degrees obtained by a FS5 analyser.

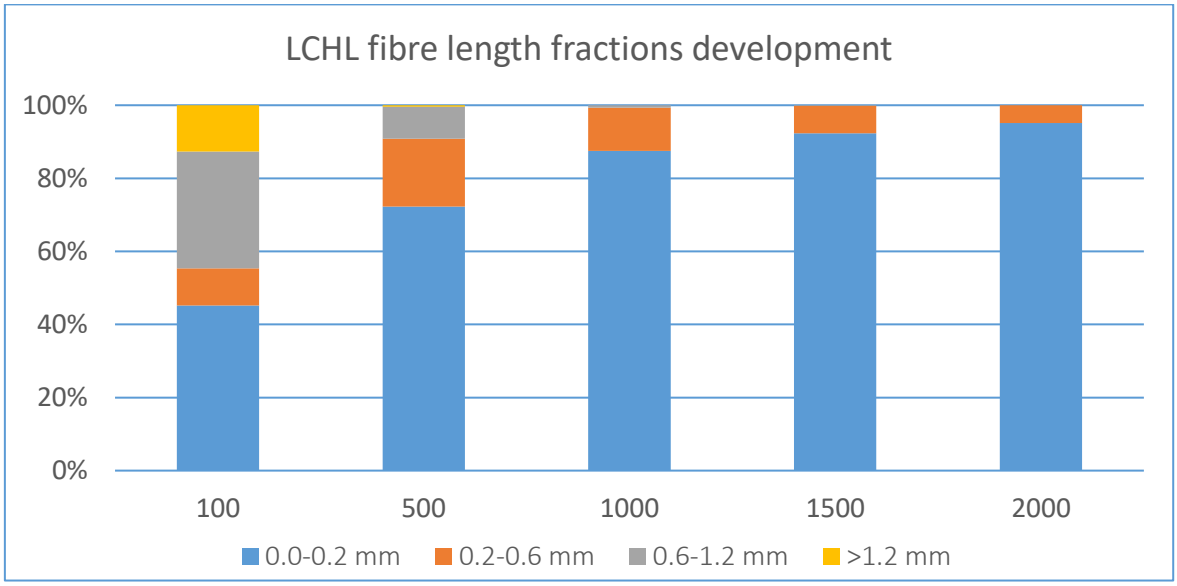

Figure 30. LCHL fibre length fractions development.

All fibre properties exhibited a strong change during the first 500-1 000 kWh/t of SEC. After that, the effects started to level off. Figure 30 illustrates how almost all of the fibres are quickly reduced to below 0.2 mm in length. Once again, light microscope images confirm the quantitative data of the fibre analysis.

Strong increase in fibrillation between SEC 1 500 kWh/t and SEC 2 000 kWh/t must contain some sort of bias. The long storage time of the pulp before fibre analysis has seemingly affected the samples differently. Some sort of impurity might have been the cause as pH and ionic balance affect the swelling and bonding of cellulose fibrils. Refining seems to affect fibre width most profoundly, as a remarkable loss in this characteristic between SEC 500 and SEC 1 000 kWh/t was observed. Same phenomenon was seen with HCHL. However, all fibre measurements are subject to the limits and settings of the equipment used. Though using state-of-the-art technology, the FS5 analyser, settings for MFC refining have not yet been optimised. Also, physical limits such as visible light wavelength limit the resolution when particle dimensions approach nanoscale.

7.2.7 Tensile tests

Tensile tests exhibited great deal of variance. Upon retesting some of the samples, it was marked that the way how mixing of MFC into the pre-refined hardwood kraft stock pulp was carried out had noticeable effect on the results. As was stated in the literature, pulp has strong tendency to form flocs even at low consistencies and ever more so with MFC. Since no standard dispersion and mixing procedure was established, this led to some degree of uncertainty with the results. Mechanical tests were done partially at Åbo Akademi and partially at Aalto University and not all dispersing or mixing equipment, like Ultraturrax or ultrasonication, was available in both locations. However, each set of tests, e.g. tensile tests with varying MFC contents or tests with cationic starch, was done in a consistent manner.

Varying storage times may also have affected the results. Mechanical tests were done over the course of some two months, which affects the quality of MFC to some degree as was later seen in fibre analysis, even though the MFC was stored in a refrigerator. No wire water analysis was done as to evaluate the retention of MFC. Thus, additive percentages used indicate the amount added to the stock pulp, not the actual load present in the sheets.

Tables 11 and 12 show tensile strength index comparisons between different refining methods and different SEC values. Reference pulp of SEC 100 kWh/t with no MFC added has clearly lower value than any other sample signifying that MFC does increase the strength of paper. However, as stated above and seen especially in the Table 12, laboratory sheet measurements were too ambiguous for insightful conclusions between different refining methods or SEC values.

Table 11. Tensile strength indices [Nm/g] at SEC 500 kWh/t with 5 % MFC added to the stock.

Reference	LCHL	HCLL	HCHL	LCLL	Pilot
76 ± 2	84 ± 2	85 ± 2	87 ± 2	89 ± 2	91 ± 2

Table 12. Tensile strength indices [Nm/g] of LCHL at various SEC values with 5 % MFC added to the stock.

SEC100	SEC500	SEC1000	SEC1500	SEC2000
76 ± 2	84 ± 2	80 ± 1	85 ± 4	86 ± 2

According to the literature, best mechanical properties are achieved by the combination of MFC and CS. Laboratory sheets with varying contents of both were prepared (Table 13). HCHL SEC 500 was used as MFC. As was suggested in the literature, cooked cationic starch was first mixed with the stock pulp and let to adsorb for 10 minutes before adding diluted and Ultraturrax-dispersed MFC. Figure 31 shows relative mechanical properties of three selected sheet grades indexed by the best of the three in each category.

Table 13. Laboratory sheets with MFC and CS.

Sample ID	Share of MFC	Share of CS	TSI [Nm/g]	Strain break [%]	Elastic modulus [GPa]
Reference	0 %	0 %	76 ± 2	3.7 ± 0.1	-
2.5MFC	2.5 %	0 %	84 ± 1	4.0 ± 0.1	4.9 ± 0.1
5.0MFC	5.0 %	0 %	82 ± 1	3.7 ± 0.1	5.3 ± 0.1
2.5CS	0 %	2.5 %	82 ± 1	3.4 ± 0.1	4.5 ± 0.1
5.0CS	0 %	5.0 %	76 ± 2	3.9 ± 0.2	3.5 ± 0.1
2.5MFC & 2.5CS	2.5 %	2.5 %	90 ± 2	4.3 ± 0.1	4.1 ± 0.1
5.0MFC & 2.5CS	5.0 %	2.5 %	94 ± 2	4.0 ± 0.2	4.6 ± 0.1

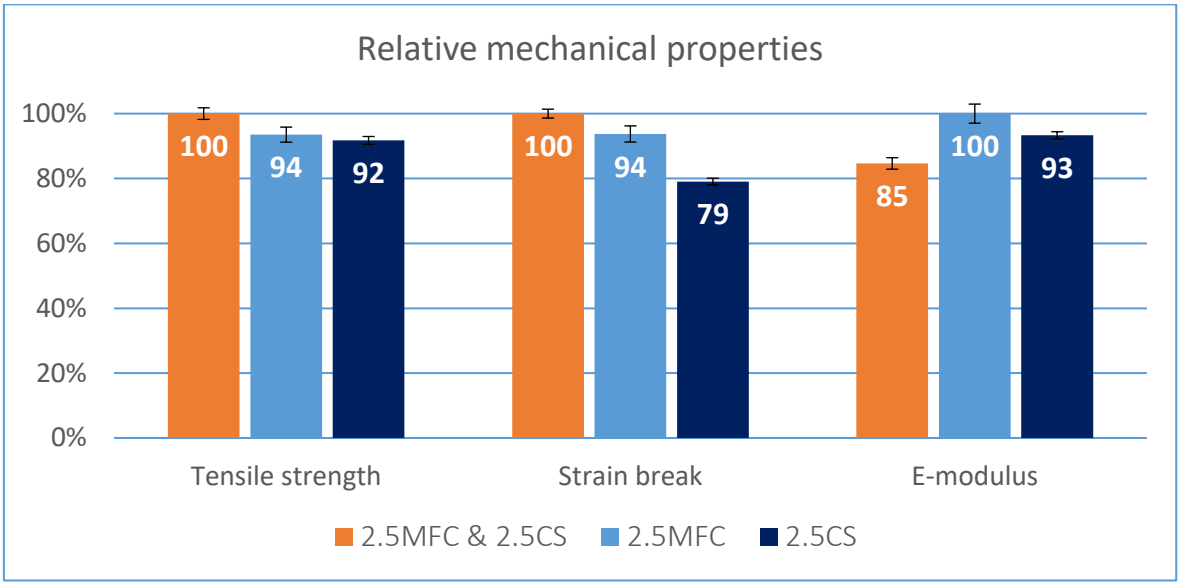

Figure 31. Tensile test results with MFC and CS.

Highest tensile index was achieved with the mixture of both additives. However, it is unclear how much of the added strength is only due to better retention of MFC by the addition of CS. Variation in results between single additive sheets is too small for definite conclusions, but 5 % of CS seems to be too much as is suggested in the literature. CS should make paper more brittle, which is indicated in the lower strain break of 2.5 % of CS but not with 5 % of CS. Already with 2.5 % of CS the paper sheets were very sticky and exhibited intense blocking with suction cartonboards during sheet preparation, which caused tearing of the sheet surface and potential strength loss.

Surprisingly, elastic modulus was substantially lower with the combination of the two additives compared to single additive sheets (Figure 31). In other tests, higher dose of MFC always led to higher elastic modulus. With CS, the effect was vice versa. Since CS was let to adsorb on the fibre surfaces first, it might be that CS governs stiffness properties. 8 % difference to the sheets with only CS might be due to random variation in the experimental conditions.

Looking at how different mechanical properties evolve when the dose of MFC or CS is increased, it can be concluded that the two function in a different way and are not merely rival strength additives but complement each other as was concluded in the literature review.

With MFC films made of the four SEC 500 pulps, no statistically significant difference in mechanical properties was observed (Table 14). Films exhibited a lot more deviation in results than paper sheets. Films were produced using a non-standard method and dispersion time varied between 10 and 15 minutes. With the pressure chamber, formation of the films was lacking. Also, due to the cumbersome preparation procedure, limited number of parallel tests could be done.

Table 14. SEC 500 film tensile test results.

Sample ID	TSI [Nm/g]	Strain break [%]	Elastic modulus [GPa]
HCHL	92 ± 16	1.5 ± 0.5	10.1 ± 0.6
LCHL	88 ± 17	1.7 ± 0.8	8.5 ± 0.5
HCLL	98 ± 23	1.8 ± 0.6	8.6 ± 0.8
LCLL	100 ± 15	1.6 ± 0.4	8.3 ± 0.7

Figure 32 shows results for tensile tests between SEC 2 500 and SEC 500 MFC from HCHL. Clear improvements with longer refining in tensile strength and strain break were observed. Lesser amount of deviation observed with SEC 2 500 is probably due to better dispersion. It was assumed, that more refined MFC requires more intensive dispersion,

thus sonication was used in addition to mixing with a magnet stirrer. It is difficult to say whether same dispersion procedure should be used with different products. Best approach would be to evaluate the effect of dispersion and mixing separately to find the intensity that gives best results for each product. However, available resources precluded such an approach.

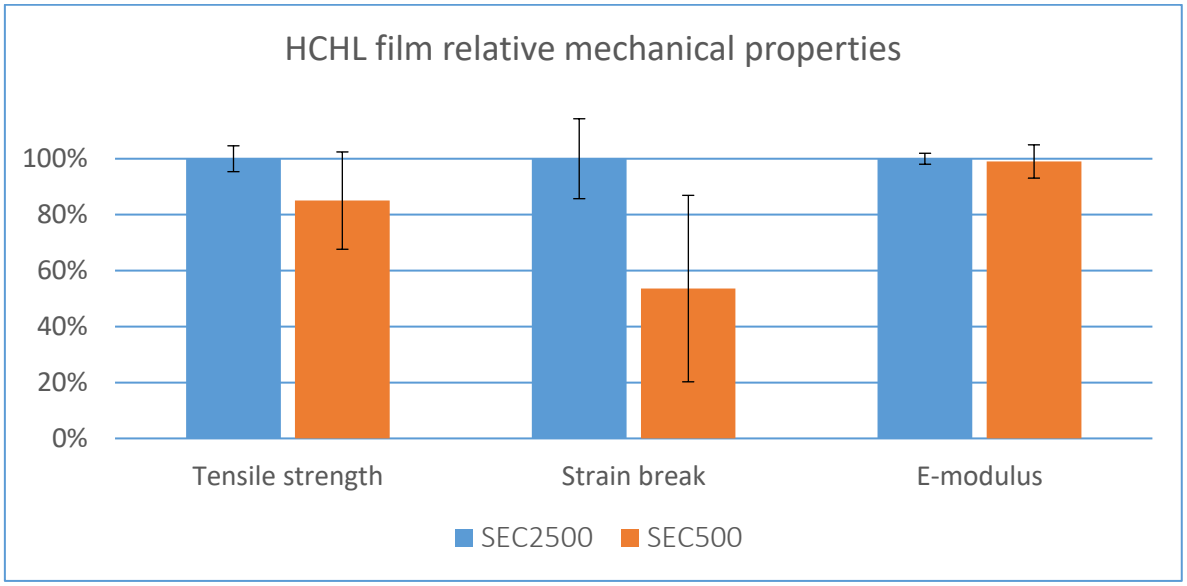

Figure 32. HCHL SEC 2500 vs. SEC 500 film tensile test results.

7.2.8 Internal bond strength

TMP laboratory sheets with 2.5 %, 5 % and 10 % of HCHL SEC 2 500 MFC as well as reference sheets with no MFC were prepared and measured for internal bond strength. As was the case with tensile tests, no analysis for actual retention was carried out. Results are shown in Figure 33. Spruce TMP with a CSF value of 35 ml from a Finnish magazine paper mill was used. Freeness of 35 ml is very low compared to CSF of around 250-500 ml that is normally used in paperboard TMP (Huusari, Lundin et al. 2009). Higher degree of refining means more fines material and fibrillation in the pulp. TMP with such a low CSF value could contain up to 40 % of fines material with poor bonding capability. Overall, this should lead to smaller difference with the addition of MFC. Still, significant improvement in the internal bond strength with the addition of only 2.5 % of MFC was recorded. The reason for drop in strength in 5 % and 10 % samples could be caused by multiple factors. Small differences in MFC disintegration and mixing into the stock pulp occurred as no

standard methods for these were established. Reference and 2.5 % MFC samples were prepared immediately after hot disintegration of frozen TMP. With the latter two samples, TMP was stored in a refrigerator overnight and no heating was used with the disintegration on the day of preparing the sheets. Also, disintegration time was shorter. This might have led to poorer mechanical properties due to latent properties, like curl and kinks, in the fibres. It is also possible that higher temperature helps MFC adsorption to TMP fibre surfaces, though the pulp was diluted extensively in room temperature water. It should be noted, that Scott Bond testing is notoriously inaccurate and high deviations in results are common.

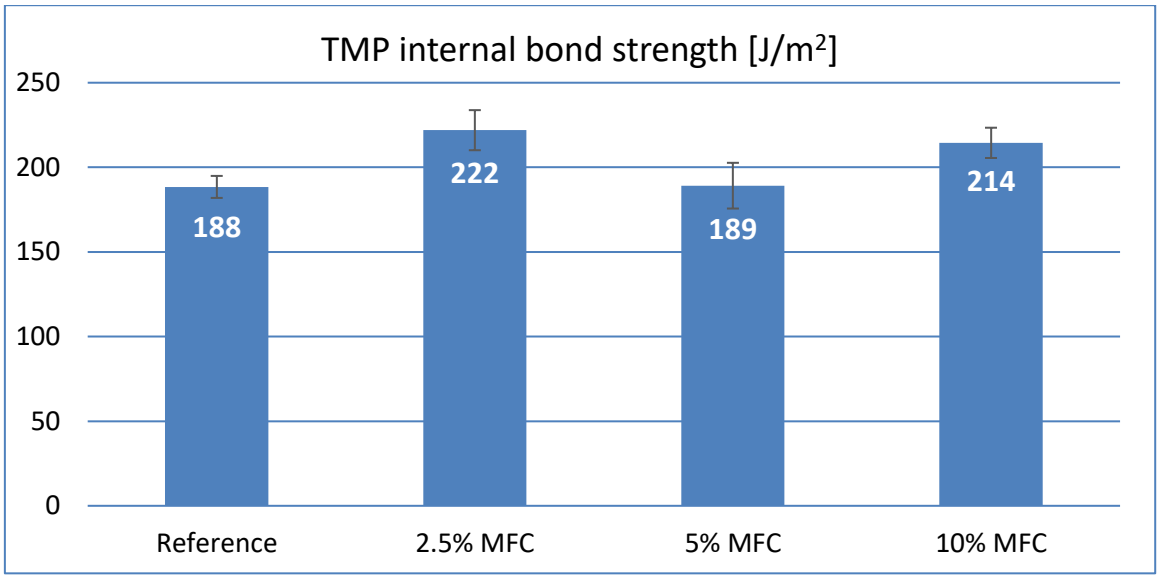

Figure 33. TMP sheet internal bond strength.

Considering the optimum load, it seems that very small portion of MFC has a significant impact on internal bond strength. Also, 10 % of MFC is clearly better than 5 %. Taking into account the above-mentioned sources of inaccuracy, cautious conclusions can be drawn that higher MFC load leads to higher internal bond strength, at least until 10 %. This is contrary to the literature, as Taipale et al. (2010) observed a levelling off of internal bond strength above 4.5 % MFC load. However, the team used chemical pulp and probably the MFC product in question was also quite different from the one used here. As the stock pulp was very highly refined and the test considered only internal cohesion of TMP, not delamination of layered structures, an optimum load for multilayer boards cannot be

suggested. However, only a certain level of internal bond strength is needed in these applications and anything above 2 % or 3 % might be wasted money.

7.2.9 Film optical measurements and SEM images

Optical measurements were done for each SEC 500 kWh/t sample (Table 15). LCHL had significantly lower opacity than the others. Rest of the samples exhibit very similar opacity, though the results follow logically those of the fibre analysis. With limited number of parallel tests, differences in whiteness are not statistically significant. Brightness seems to be very even between the samples. The findings are in line with fibre analysis as smaller particle size leads to more see-through film.

Table 15. SEC 500 kWh/t film optical properties.

Sample ID	Whiteness	ISO Brightness [%]	Opacity [%]
HCHL	119 ± 2	89 ± 0.5	43 ± 1
LCHL	126 ± 2	90 ± 0.5	36 ± 2
HCLL	121 ± 2	90 ± 0.5	45 ± 1
LCLL	118 ± 1	89 ± 0.3	44 ± 1

SEM-images of the SEC 500 kWh/t films show a dense network of fibrils jabbed by bigger fibres refined to various degrees here and there (Figure 34). Figure 35 shows that some fibrils are in the nanoscale. Starting from the top right corner of the image, a fibre is teared from one end into smaller and smaller tendrils. Figure 36 is taken from the SEC 2 500 kWh/t HCHL sample. Between the dense network of microfibrils and fibre particles are areas that seem to be jellified fibril material. Fibril dimensions in these areas are most probably in the nanoscale.

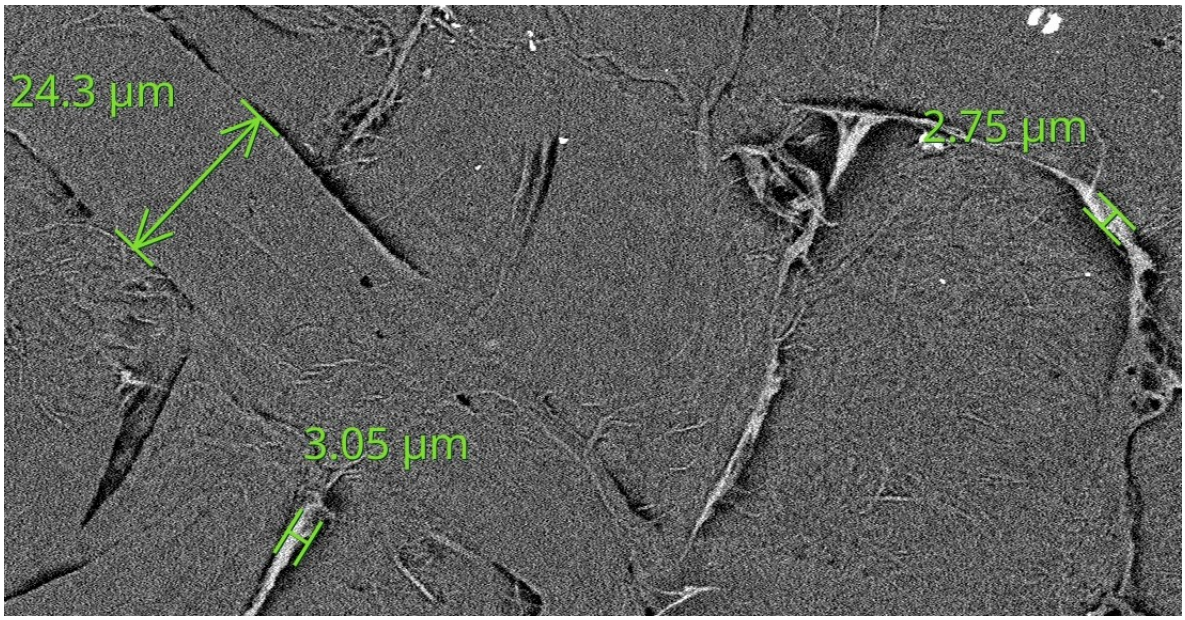

Figure 34. SEM image of SEC 500 kWh/t HCHL film, 910x magnification.

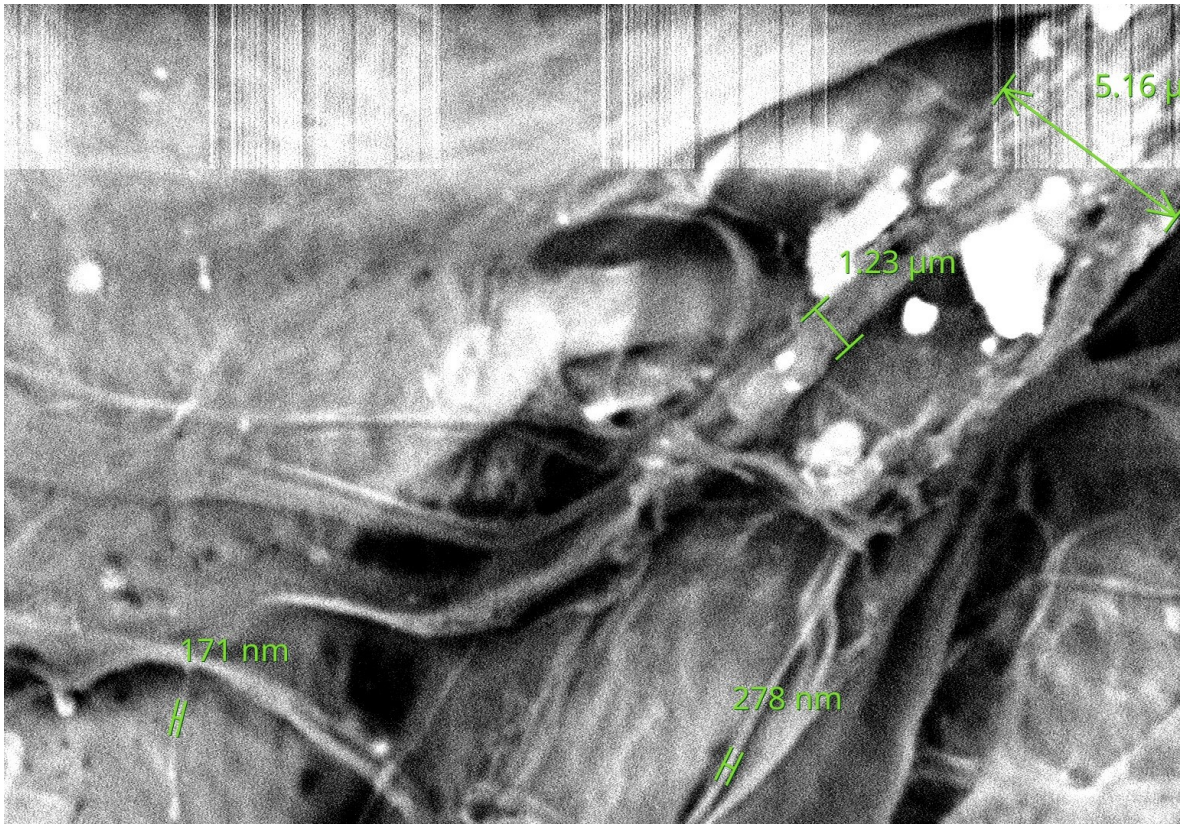

Figure 35. SEM image of SEC 500 kWh/t LCLL film, 7100x magnification.

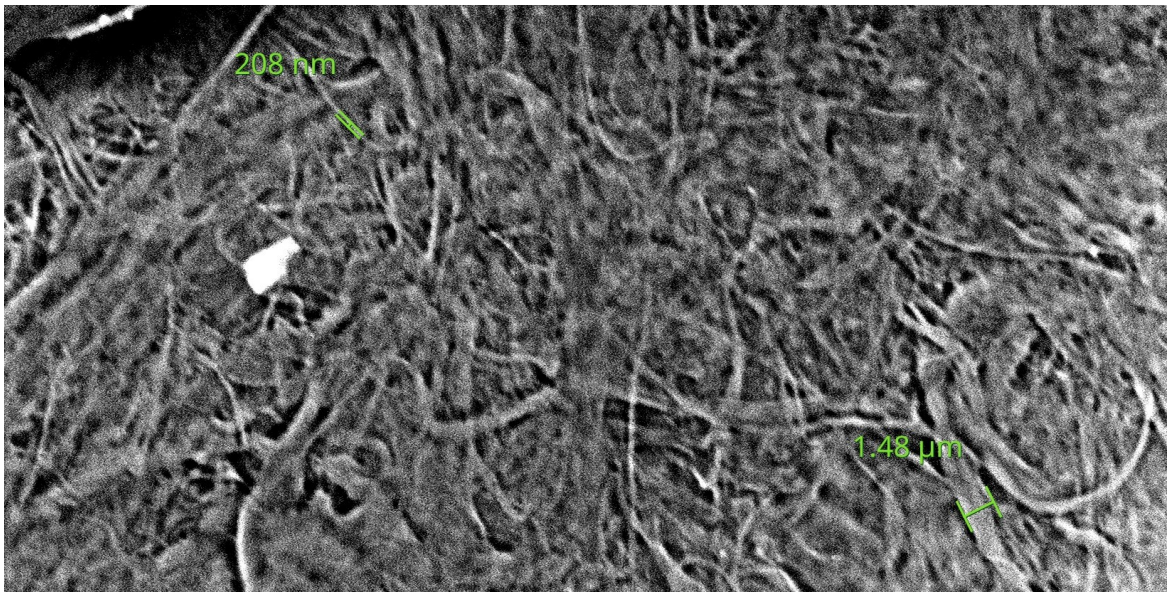

Figure 36. SEM image of SEC 2500 kWh/t HCHL film, 4000x magnification.

SEC 500 kWh/t and SEC 2 500 kWh/t samples were also freeze-dried for SEM imaging. Figure 37 shows areas that might be teared fibres or dense networks of fibrils in nano- and microscale. Zooming in the apparent gel-like parts of SEC 2 500 kWh/t HCHL reveals ever finer fibril network until the limit of resolution (Figure 38).

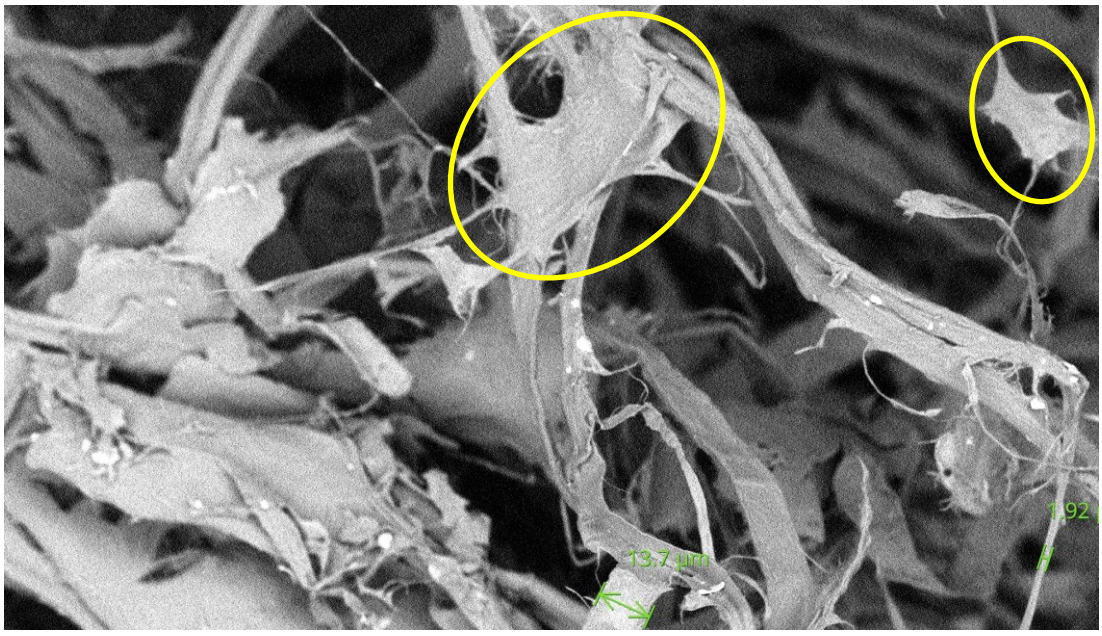

Figure 37. SEM image of SEC 500 kWh/t freeze-dried HCLL, 970x magnification.

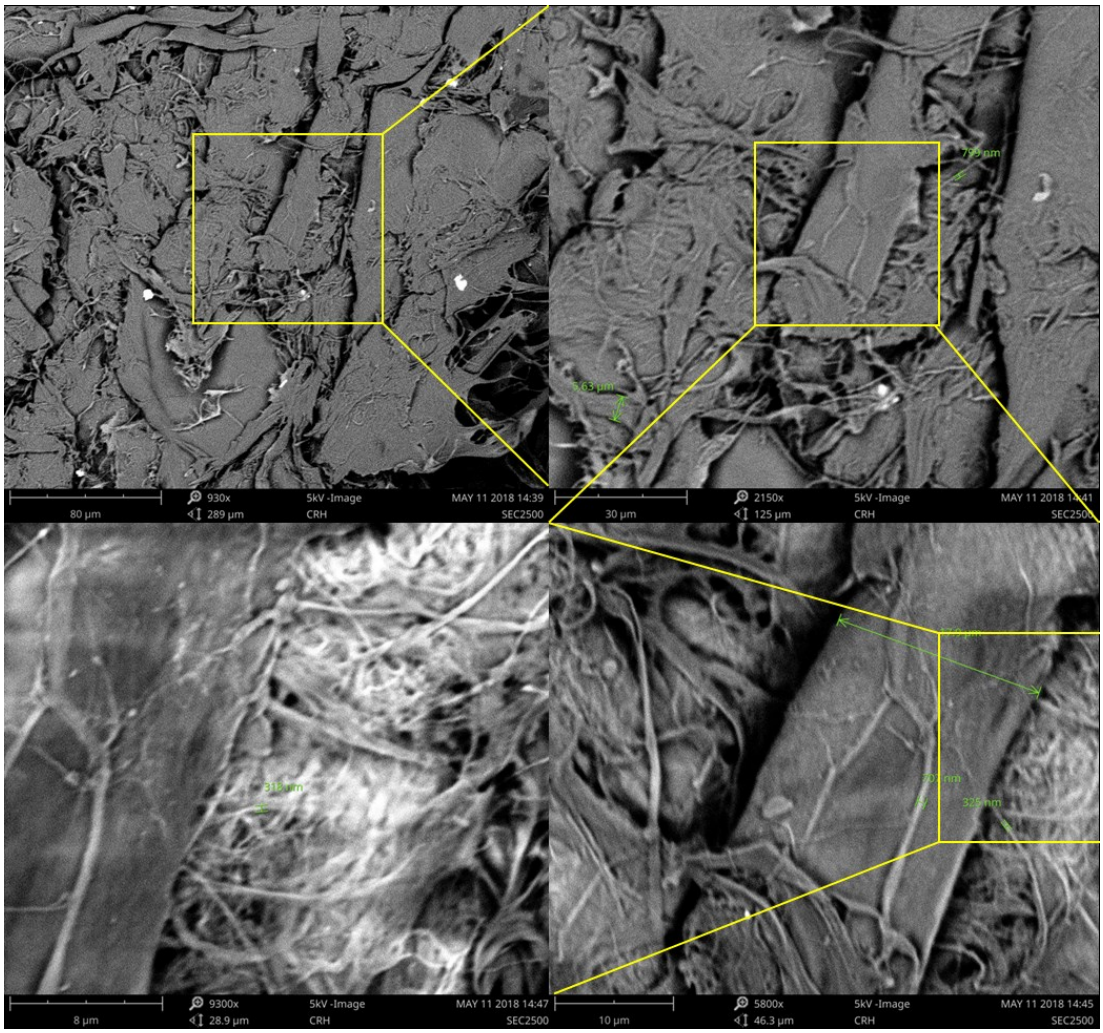

Figure 38. SEM image of SEC 2500 kWh/t freeze-dried HCHL, 930-9300x magnification.

Optical and SEM imaging confirm that a highly fibrillated material with occasional whole fibres was produced. Fibril network seems to be the dominating phase. Stray fibres should be of no problem in a paper or board network as long as the fibrillated bulk of the material is efficiently mixed and dispersed in the matrix.

7.2.10 Rheometry

Figure 39 shows the shear stress diagrams for LCHL samples taken from the whole range of refining and for the end-products of both pilot trials. All measurements were done mixing 3 % MFC into unrefined pulp. Figure 40 shows viscosity for the same samples.

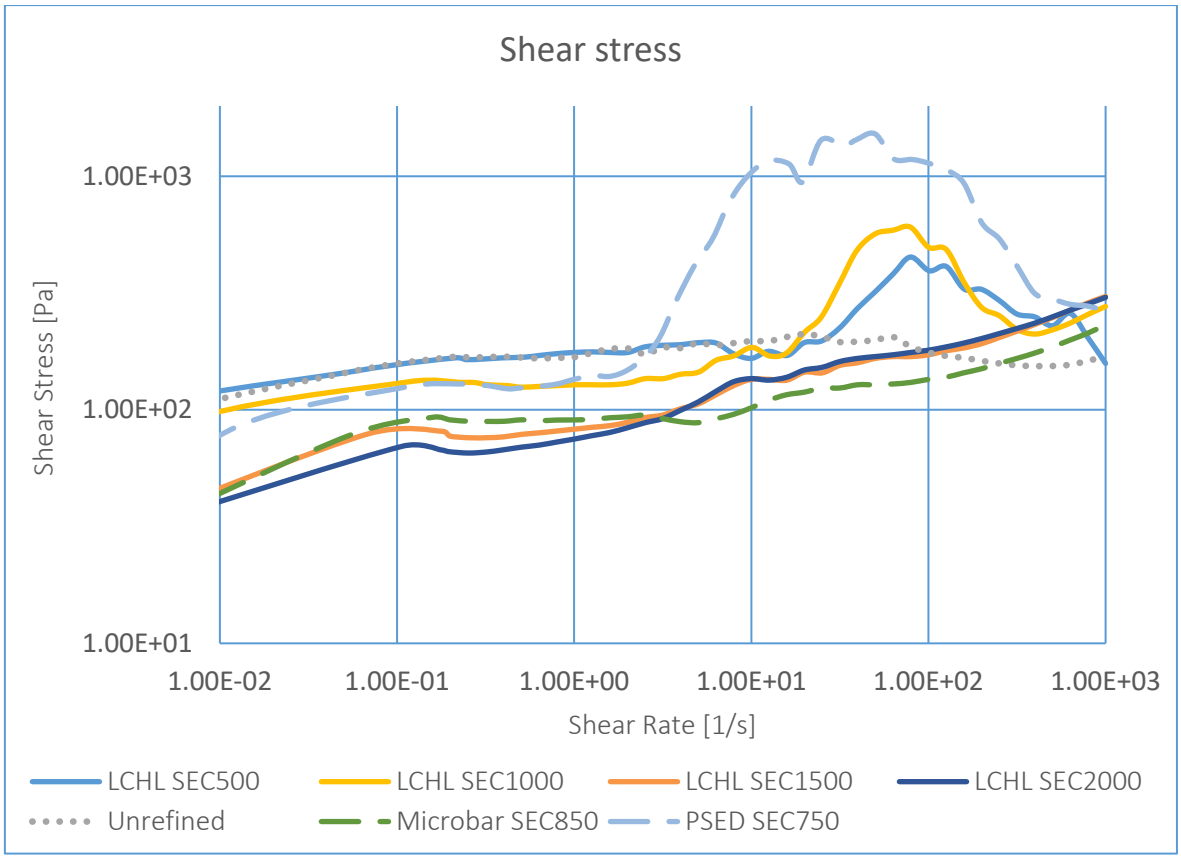

Figure 39. Shear stress development of LCHL and comparison to pilot trials.

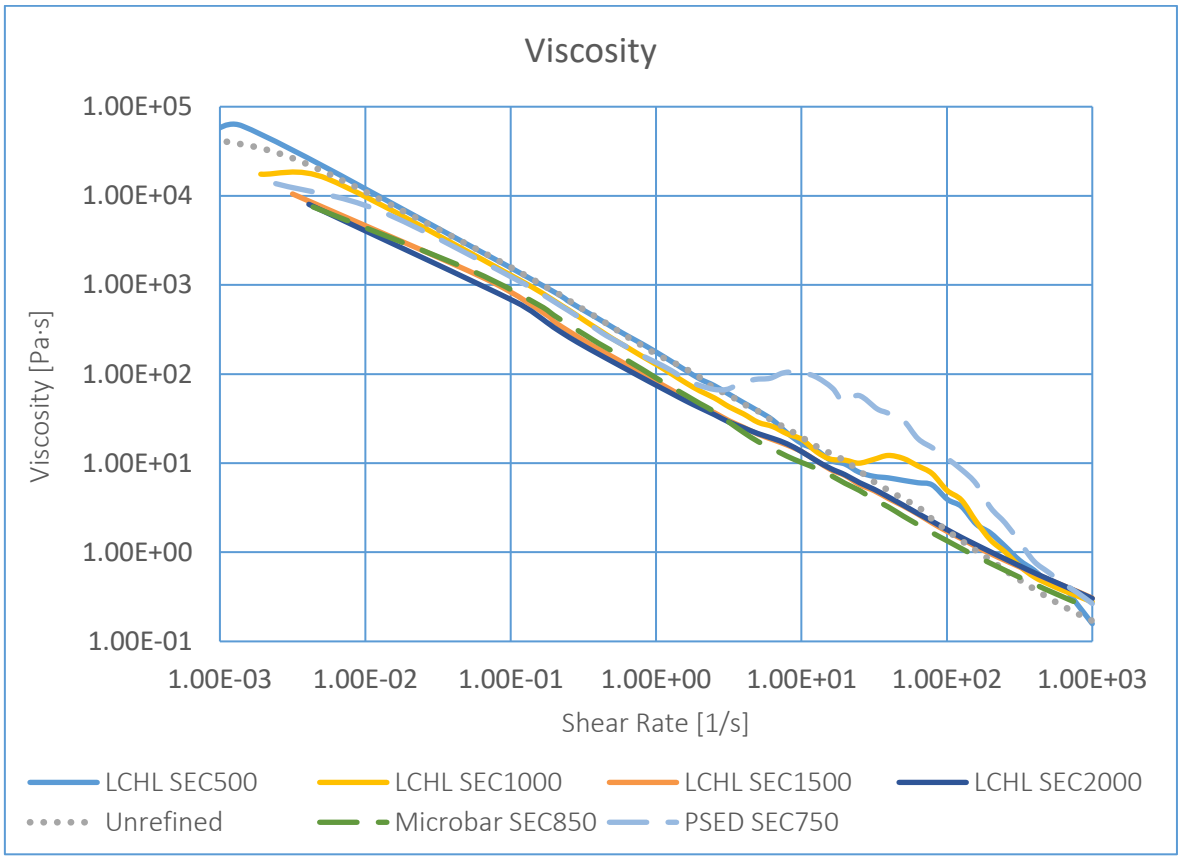

Figure 40. Viscosity of LCHL samples and both pilot trials.

Unrefined pulp without any MFC got separated into water phase and suspension in the rheometer. Thus, the curve for unrefined pulp reflects more the rheology of water than pulp. Something curious happens in the pulp around SEC 500-1000 kWh/t depending on the refining characteristics, as LCHL SEC500, SEC1000, and PSED exhibit a certain bump peaking at shear rate of around 60 s^{-1}. Probably the fibres that are still present form, together with the fibrillated material, a network that starts to break at certain shear rate requiring more pressure at that point, displayed by the higher shear stress or viscosity. Once almost all of the fibres are cut into smaller pieces, rheology of the material starts to exhibit more even behaviour. Rheometric results further confirm the favourable refining outcome with Microbar fillings. Laboratory trials required almost double the energy consumption for similar flow behaviour. It should also be noted, that after this point of nearly even flow behaviour was reached, no major difference between the LCHL SEC1500, SEC2000, and Microbar SEC850 was observed.

7.3 Discussion

In this chapter, some aspects of characterization and the differences between laboratory and pilot trials are discussed more deeply.

7.3.1 Characterization

Fibre analysis provided invaluable data where tensile tests lacked precision. SR value was found to be an overall good indicator for the level of fibrillation in the beginning of refining, but losing its accuracy as the values approached 90. Internal bond measurements, optical measurements, and rheology tests all gave valuable insight.

At some point of prolonged refining, SR started to decrease. Figure 41 shows the development of SR value as line diagram and corresponding share of over 0.6 mm long fibres as area for LCHL and pilot trial. It might be that as long as the pulp contains sufficient amount of fibres large enough to form a mat on the SR wire, most of the micro- and nanofibrils are trapped holding the water in place. After prolonged refining, more and more fibrils pass through the wire. Presence of fibrils in the wire water was perceivable by

naked eye with the highly refined samples. This leads to conclusion that traditional freeness measurement is suitable only during the very beginning of refining but loses its accuracy as the fibre dimensions decrease.

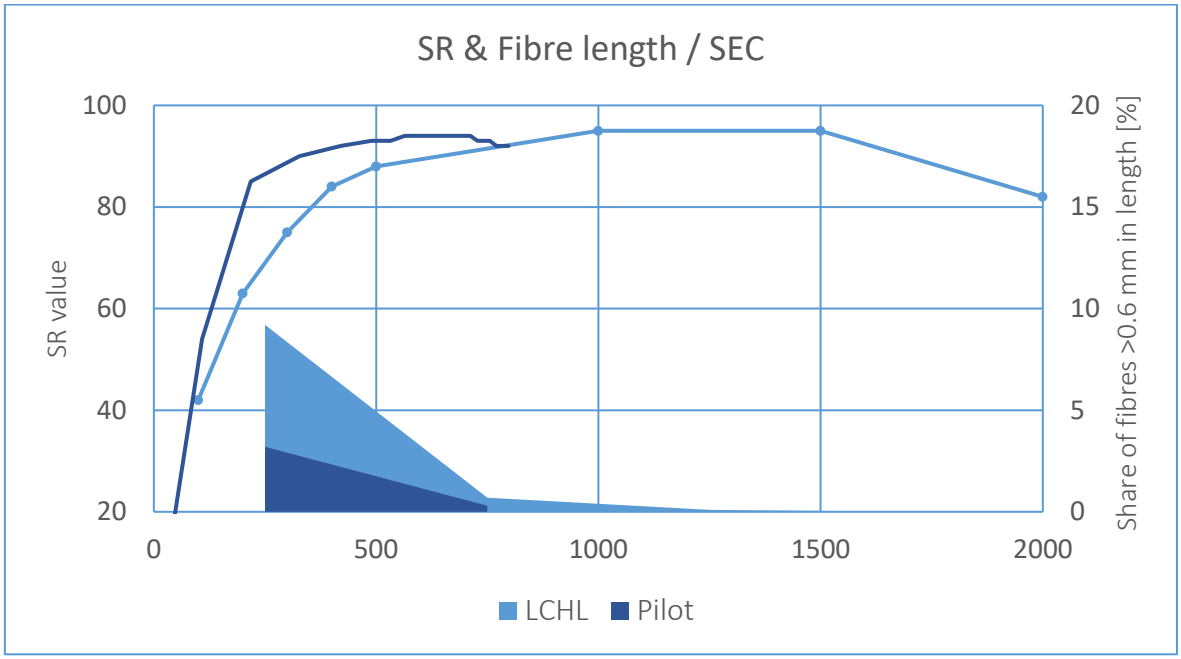

Figure 41. Development of SR and fibre length.

7.3.2 Pilot trials versus laboratory trials

As was concluded in the section *7.2.3 ProLab™ trials with revised experimental design*, high SEL is a precondition for successful MFC refining. Though ProLab™ seemed to outperform pilot trials with JC-01 in this regard (Figure 22), fibre analysis proved otherwise. Reasons why SEL is not the best indicator of successful MFC-refining for a comparison between laboratory and pilot scale are the differences in scale, fillings configuration, run parameters, and materials. JC-01 fillings are many times larger than those of ProLab™. Even though ProLab™'s refiner was run at a rotation speed of 3000 rpm compared to 1200-1400 rpm with JC-01, the tangential velocity with the former was 8-19 m/s and 17-37 m/s with the latter. Beating of fibres with double the speed of ProLab™ probably gave and edge to pilot trials in terms of fibrillation and fibre dimension reduction. Also, ProLab™ had a flow speed of around 50-60 l/min compared to 900 l/min

in pilot runs. Other variables between laboratory and pilot trials that should be noted are different pulp and variations in temperature and pressure.

Pilot trials were promising also considering the configuration of an industrial scale MFC plant. In the beginning, over 100 kWh/t of SEC was achieved with each pass. Since JC-01 is one of the smallest industrial scale refiners available, a larger one would allow much higher SEC with each pass. Also, if the main engine of JC-01 in the pilot plant had been more powerful, higher SEC in the first passes had likely been possible. Probably a continuous production line with three to four different refiners with fillings optimised for each step would be enough to produce MFC-like pulp with sufficient strength enhancement properties. SEC 500 kWh/t with a conservative energy efficiency of 60 % would correspond to a price of energy of around 50 €/t (*Equation 8*) (IEA 2016).

Equation 8. Price of energy for SEC 500 kWh/t MFC.

$$500\,\frac{kWh}{t} * \frac{1}{0.6} * 0.06\,\frac{€}{kWh} \approx 50\,\frac{€}{t}$$

7.4 Conclusions

The purpose of this thesis is to proof that a continuous, commercial production of microfibrillated cellulose by refining for papermaking applications integrated to a mill is feasible. According to literature, refining is most reasonable mechanical production method compared to others such as homogenization in terms of energy consumption and scalable equipment. Feasibility of pre-treatments with chemicals, enzymes, or other means was assessed only in the literature review, but the gathered evidence indicates that such procedures are not necessary. Comparison to starch revealed that MFC is not merely a rival strength enhancement agent, but the two complement each other and best results are attained by the combination of both. Effects of hornification do not seem to be of concern, and some fibre properties are even better suited for the target applications with dried than neverdried pulp. Overall the produced MFC increased the mechanical properties of chemical pulp and TMP implying that it is indeed beneficial to use the additive in these applications.

Fibre analysis, mechanical tests, and development of various process parameters during refining all indicate that the efficiency of refining starts to level off rather quickly, though huge differences between laboratory and pilot trials were seen. Until specific energy consumption of around 500 kWh/t refining can be done with a high coefficient of efficiency. In laboratory, refining could be continued until SEC 2 500 kWh/t without any technical challenges. Yet, the effects on fibre properties compared to the energy consumption after SEC 1 000 kWh/t were minimal. It seems that continuing refining far beyond SEC 500 kWh/t is not practical. Whether this kind of pulp product can be called microfibrillated cellulose is a fair question and depends on terminology as much as on the efficiency of refining. Specific energy consumption as itself does not tell much about the product, but if refining is at least as effective as it was in the laboratory and pilot trials at their best in the experiments done here, a product that is at least mostly MFC is produced. Though a fair amount of larger fibres is left in the product, this should not be a problem considering papermaking applications.

Specific energy consumption of 500 kWh/t is not that much of a limit in terms of energy consumption. With as good energy efficiency as was achieved in this work, the price of total energy consumption would be only around 50 €/t – even lower than the lowest value of around 100 €/t found in the literature. Rather, higher degree of refining sets demands for process configuration. As was concluded in the literature review, multiple passes through a refiner or having several refiners in series is required for the desired degree of fibrillation and sufficient homogeneity. With a small JC-01 industrial refiner, five passes were required for SEC 500 kWh/t. A larger refiner could drop this figure to two or three. This means, that refining could be done continuously with e.g. three refiners, optimised for each step. Unless exceedingly better equipment and highly optimised process conditions are developed, any SEC value well above 500 kWh/t would probably mean that some kind of feedback loop for pulp around the refiners is required. Thus, process configuration becomes more complicated and expensive. Without any screening methods, also the homogeneity of the product suffers.

Finding the optimal parameters; consistency, edge load, SEC, flow speed, etc., is case specific for sure and a thorough examination for each with the pulp product, end-product, and overall techno-economic situation in mind is needed if an industrial scale plant is to be built. However, certain parameters for MFC refining of hardwood kraft pulp with equipment similar to those used in chemical pulp refining without any chemical or enzymatic treatment can be recommended based on this thesis.

Fibre analysis indicates strongly that refining done in low consistency and with a high edge load produces best results. Fibre length, length fractions, and freeness measurements gave unambiguous results in the favour of these parameters. Fibrillation, fines percentage, and fibre width were more open to interpretation with some of the samples. Tensile strength of papers with certain load of MFC and MFC film optical and mechanical properties were mostly too similar or exhibited too much deviation for valid conclusions.

Consistency of about 3-4 % seems to be ideal. Laboratory trials done in 3.5 % consistency performed better than those done in 5.5 % or 6.1 % consistency. No loss in energy efficiency was observed by the reduction of consistency, though available equipment set limits for the assessment of this aspect. Lower consistency enables more fibre-refiner bar collisions instead of fibre-fibre collisions. Latter might lead to better internal fibrillation, but turning cellulose fibres into microfibrils requires contact with a hard and sharp surface.

In laboratory and pilot runs, using maximum possible edge load without breaking the equipment produced better results than lower load. As was indicated in the literature, more fibre cutting compared to other physical changes occurred with higher load, but nothing indicated that fibre cutting had gone too far. Of course, with more robust equipment it might be possible to cut the fibres too much in length which can hamper further refining as the advancing refiner bars do not catch short fibres as easily as longer ones. Wear of equipment might also cause problems in the long run. Still, higher load leads to more fibrillation and better energy efficiency.

Optical characterization methods proved their value in the assessment of different refining methods and MFC product properties. State-of-the-art automated optical fibre analysers should yield enough information for a controlled, continuous production of MFC, if interpreted carefully and with expertise. However, as the fibril dimensions approach nanoscale, usability of traditional characterization techniques is hindered. Visible light wavelength sets limits for optical assessment and freeness measurements lose their reliability when majority of the material is small enough to pass through the wire. Development of the existing analysers and novel characterization techniques are needed for a comprehensive understanding of a pulp product with dimensions approaching nanoscale. It is thrilling to see that such methods are being developed, as one such technique was used, though the results could not be published in this thesis. Rheometry seems to be too cumbersome and expertise-requiring to be considered for a mill environment unlike supposed in the conclusions on literature.

MFC seems to have a “best before” date, as fibrillation values measured with optical fibre analyser dropped significantly in the course of some two weeks. Whether this was more due to measurement technology and settings or actual MFC properties remains a question, but something clearly happens to MFC when it is stored. Literature review revealed major challenges in drying and re-dispersing of MFC. These findings both back up the conclusion that it is best to produce MFC on-site.

Much to be developed remains. These experiments were done with Finnish birch kraft pulp in specific conditions and with specific equipment, and more research is needed for a broad understanding of MFC refining in different circumstances. Logical next steps would be further optimisation of refining parameters on the basis of what was learned e.g. using high edge load and consistency of around 3-4 %, and evaluating the end-product qualities around SEC 300-700 kWh/t. It is clear that refiner fillings can be further optimised, though traditional fillings patterns were surprisingly efficient. It is also important to try MFC refining with larger industrial refiners and find the reasons and solutions for what makes this type of refining easier in laboratory scale compared to industrial scale. After assessing the process with larger refiners, sketches for process

design followed by a thorough economic analysis would be logical. As for the economic analysis, optimum load of MFC must be evaluated case specifically. Such assessment was not done in this thesis, but certain limits for maximum load were found. These include challenges in water removal, the hygroscopicity and dimensional instability of MFC, efficient dispersion, and possible complications with stock rheology.

Though the experiments indicated that pre-treatments are not required, it would be worth testing if some chemical or enzyme would be beneficial. Perhaps a small fraction of certain agent would lead to huge improvements in MFC properties but once diluted with the main stock, its effects to the end-product would be insignificant. Purely speculatively speaking, as no literature reference or experimental work on this was reviewed, it would be interesting to try e.g. carbonic acid in facilitation of fibre disintegration and neutralising it before dispersion into the main stock with calcium hydroxide to produce precipitated calcium carbonate inside the fibril matrix.

Considering characterization and testing procedures used in this work, several improvements could be made. Establishing a standard, efficient mixing and dispersion procedure for MFC in laboratory sheets is crucial. A wire water analysis for MFC retention determination with and without cationic starch or any other additives would be highly recommended. Also, using cartonboard TMP instead of magazine paper TMP for the evaluation of internal bond strength is advised. Cationic starch could be added to these measurements as well. As for the characterization, sedimentation speed might be a good additional tool for analysis. Also, if more time was concentrated on SEM imaging, phenomena in the nanoscale could be better understood. Lastly, it would be very interesting and highly useful to compare the produced MFC to commercially available options, like GL&V's MFC.

Overall, the targets set for this thesis were met. With little more luck in the laboratory trials, there would have been more time to double-check certain results and proceed further with overall optimisation of the process. Especially the experimental part contributes to existing literature, as the effects of refining parameters and different

fillings patterns are rarely published. Also, the literature review offers a solid theoretical package for MFC refining ranging from fibre physics to common concepts in refining. The findings of both literature review and experimental part support that a continuous, commercial production of microfibrillated cellulose by refining for papermaking applications integrated to a mill is feasible.

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Appendix A – FS5 parameter descriptions

Lc(l), mm: Length-weighted average fiber length.

Fines A %: Flake-like fines (type A) as percentage of the projection area of measured particles. Particles shorter than 0.2 mm are included in fines A.

f1…f6(l) %: Fractions 1–6 as percentage of lengthweighted distribution.

Fraction 1: 0–0.2 mm, width ≥ 10 µm.

Fraction 2: 0.2–0.6 mm, width ≥ 10 µm.

Fraction 3: 0.6–1.2 mm, width ≥ 10 µm.

Fraction 4: 1.2–2.0 mm, width ≥ 10 µm.

Fraction 5: 2.0–3.2 mm, width ≥ 10 µm.

Fraction 6: 3.2–7.6 mm, width ≥ 10 µm.

Fibrillation %: Projection area of fibrils in relation to the projection area of the entire object, scaled into a Percentage.

Appendix B – Original experimental design

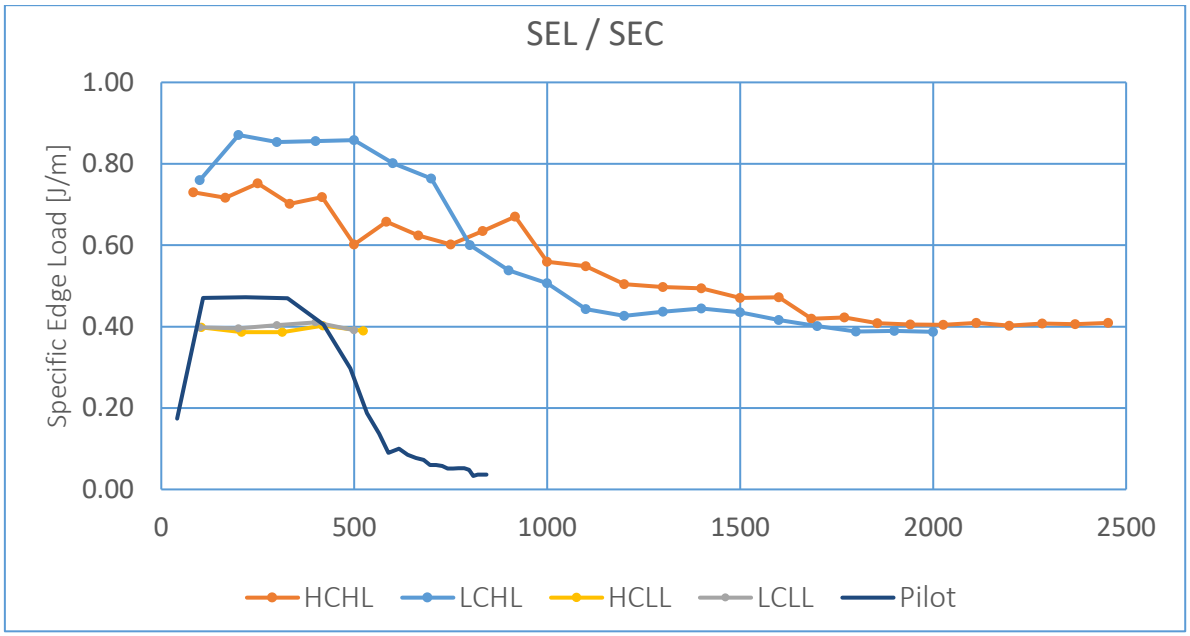
KOEAJOT							
Aika	**Aika (kum.)**	**Pvm**	**Missä**	**Kuka**	**Koeajon tarkoitus**	**Muuttujat**	**Ajot**	**Kommentit**
1.5 pv	1.5 pv	12/03	Åbo	E&V	1. Uuden erän sisäänajo	Teho	Teho 1 Teho 2 (Hiekoitus)	Kokeillaan uutta erää eri teholla/paljonko saadaan tehoja irti, kuinka pitkälle voidaan ajaa ilman terille menoa, mahdollinen hiekoitusajo. Huom! Näistä ajoista voisi lähettää 1-2 näytettä Kajaaniin, varmistetaan ismolta onko tälle tarvetta/onnistuuko.
	1.5 pv							
1.0 pv	2.5 pv	13/03	Åbo	E&V	2. Virtausnopeus	Virtausnopeus	30 l/min 60 l/min	Kokeillaan virtausnopeuden vaikutusta tehoon, massan ominaisuuksiin sekä ajettavuuteen/näytteenottoon, valitaan teho sisäänajon perusteella (oletus noin 5 kWh), sakeus 3 %
	2.5 pv							
2.0 pv	4.5 pv	15/03	Åbo	E&V	3. Maksimisakeuden selvitys	Sakeus	6 % (5 %) (4 %)	Kokeillaan ajaa 6 % sakeudella, lasketaan tarvittaessa alemmas, verrataan edellisiin 3 % ajoihin SEC:in ja massan ominaisuuksien kannalta, virtausnopeus edellisten ajojen perusteella (oletuksena 30 l/min)
	4.5 pv							
1.5 pv	6.0 pv	19/03	Åbo	E&V	4.1 Tehon vaikutus	Teho	Teho 1* (SEM) Teho 2*	Sakeus 3 %, virtausnopeus edellisten ajojen perusteella (oletuksena 30 l/min), tehot sisäänajon perusteella noin välillä 3-6 kWh - arvoltu optimiteho sekä yksi tätä alhaisempi ja yksi tätä korkeampi teho. *) otetaan massaa talteen tarkempia mittauksia varten (lopputuote sekä varmuuden vuoksi 1 välinäyte noin puolesta välistä tavoite-SEC:tä), valmistetaan 3 kpl labra-arkkeja/näyte ajojen aikana. SEM-kuvat alkutilanteesta, ekojen läpäisyjen jälkeen (SEC 100-200), noin puolessa välissä ja lopputuotteesta ajoille 4.1.1 ja 4.1.3.
	6.0 pv							
	6.0 pv						Teho 3* (SEM)	
1.5 pv	7.5 pv	20/03	Åbo	E&V	4.2 Tehon vaikutus	Teho	Teho 1*	Maksimisakeus (4-6 %), muuten sama kuin yllä
	7.5 pv						Teho 2*	
	7.5 pv						Teho 3*	
1.5 pv	9.0 pv	22/03	Åbo	E&V	5. Kesken ajon laimennus	Teho	Teho X*	Valitaan edellisten ajojen perusteella kaksi lupaavinta tehoa, laimennus maksimisakeudesta -> 3 % kun SR ylittää arvon 80
	9.0 pv						Teho Y*	
1.0 pv	10.0 pv	23/03	Åbo	E&V	6. Tehon lasku kesken ajon	Sakeus/ laimennus	Ajo 1* Ajo 2*	Valitaan aiemmista ajoista kaksi sakeutta tai laimennusajoa, jotka valkuttavat eniten hyötyvän mahdollisesta tehon alentamisesta kesken ajon, alku- ja lopputeho edellisten ajojen perusteella esim. max teho -> 4 kWh, kun SR ylittää 80

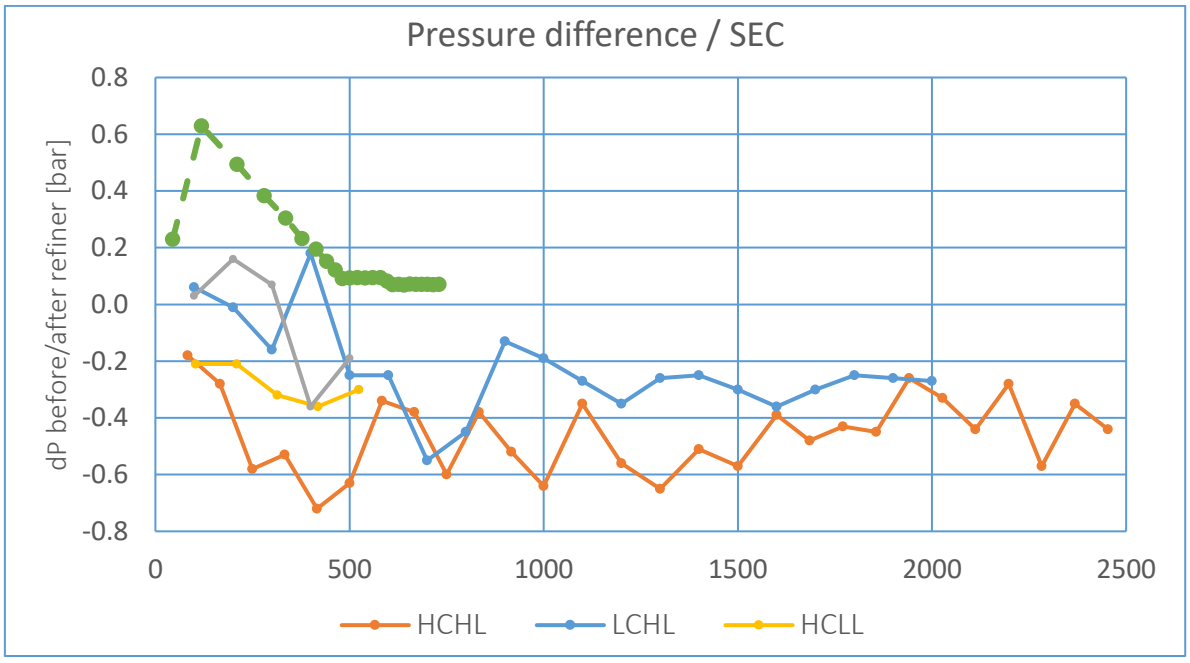
KARAKTERISOINTI							
Aika	**Aika (kum.)**	**Pvm**	**Missä**	**Kuka**	**Mitä testataan**	**Menetelmät**	**Testien määrä**	**Kommentit**
2.0 pv	12.0 pv	26.03	Åbo/Aalto	E&V	Lujuus	Labra-arkit (valmiina), tensile	11 testiä (10-20 näytettä/testi)	Oletuksena 5 wt% MFC:itä per arkki, drainage-ajan mukaan voidaan nostaa tai laskea tätä. Testeihin tarvitaan 10-20 15mm liuskaa, yhdestä arkista saa 10-15 kpl eli 3 arkkia per näyte riittää hyvin. Arkit tehty valmiiksi ajojen 4.1-6 aikana. Mukana myös referenssinäyte ilman MFC:itä.
2.0 pv	14.0 pv	28.03	Åbo/Aalto	E&V	Lujuus, MFC vs. kationinen tärkkelys	Labra-arkit, tensile	5 testiä (10-20 näytettä/testi)	2 parasta massaa aiempien testien perusteella, verrataan kahtena eri pitoisuutena (esim. 5 % ja 10 %) kationiseen tärkkelykseen (samat pitoisuudet) sekä 2 % CS + 5 ja 10 % MFC. Käytetään edellisiä tuloksia 5 % MFC:lle.
1.0 pv	15.0 pv	30.03	Åbo/Aalto	E&V	Repäisylujuus	Labra-arkit, tear	n. 5 testiä (10-20 näytettä/testi)	Repäisylujuustestit valituille näytteille ylimääräisistä arkeista.
2.0 pv	17.0 pv	03.04	Aalto	V	Z-strength TMP:n lisäaineena	Labra-arkit, tensile	3-4 testiä (10-20 näytettä/testi)	Paras massa kahtena eri pitoisuutena, paras CS pitoisuus (ja paras CS + MFC yhdistelmä jos parempi kuin jompi kumpi pelkästään) TMP:n lisäaineena
1.0 pv	18.0 pv	-	Åbo	E&V	Kuitujen ominaisuudet	Valomikroskopia	muutamia	Valituista näytteistä kuvia valomikroskoopilla, muun ehtimisen mukaan.
1.0 pv	19.0 pv	-	Åbo/Aalto	E&V	Vedensitomiskyky	WRV	muutamia	Valituista näytteistä WRV, muun ehtimisen mukaan.
1.0 pv	20.0 pv	Huhti	Kajaani	E&V	Kuitujen ominaisuudet	FibreLab	max 10	Max 10 lupaavinta näytettä (ajoista 4.1-6) mukaan Kajaaniin, voidaan myös jättää turhalta vaikuttavia näytteitä pois.
5.0 pv	25.0 pv	Huhti	Aalto	V	Optiset, density, SEM, (tensile)	Filmit	max 3 näytteestä 4 filmiä/näyte	Parhaista näytteistä filmit, käytettävissä olevan ajan mukaan ensin optiset testit ja mahdollisesti tensile testit

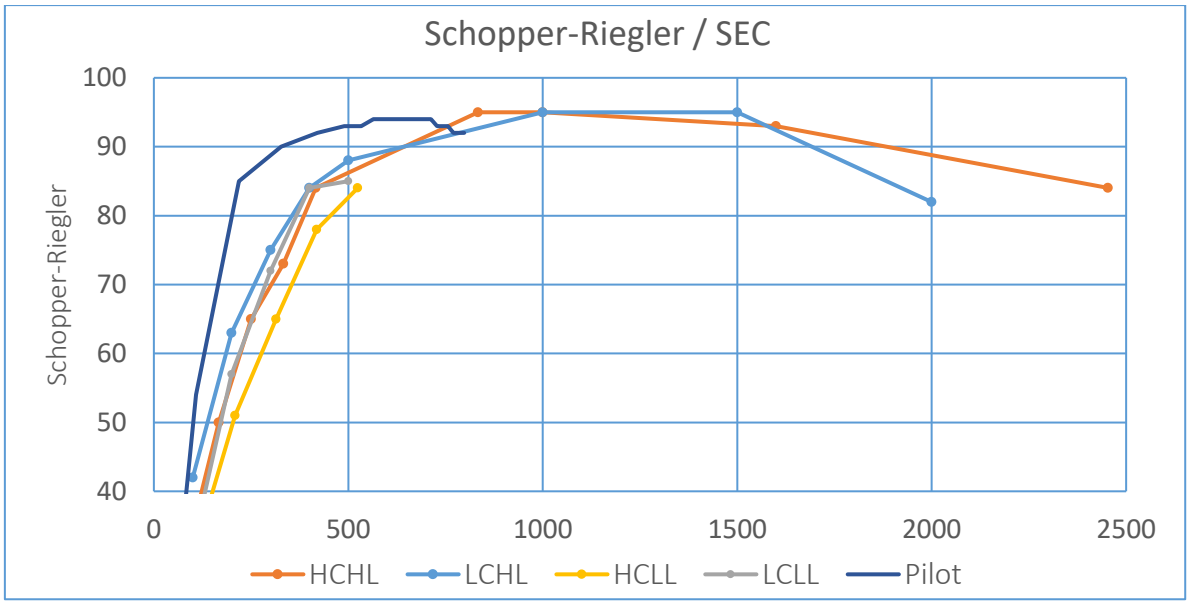
Appendix C – Revised experimental design

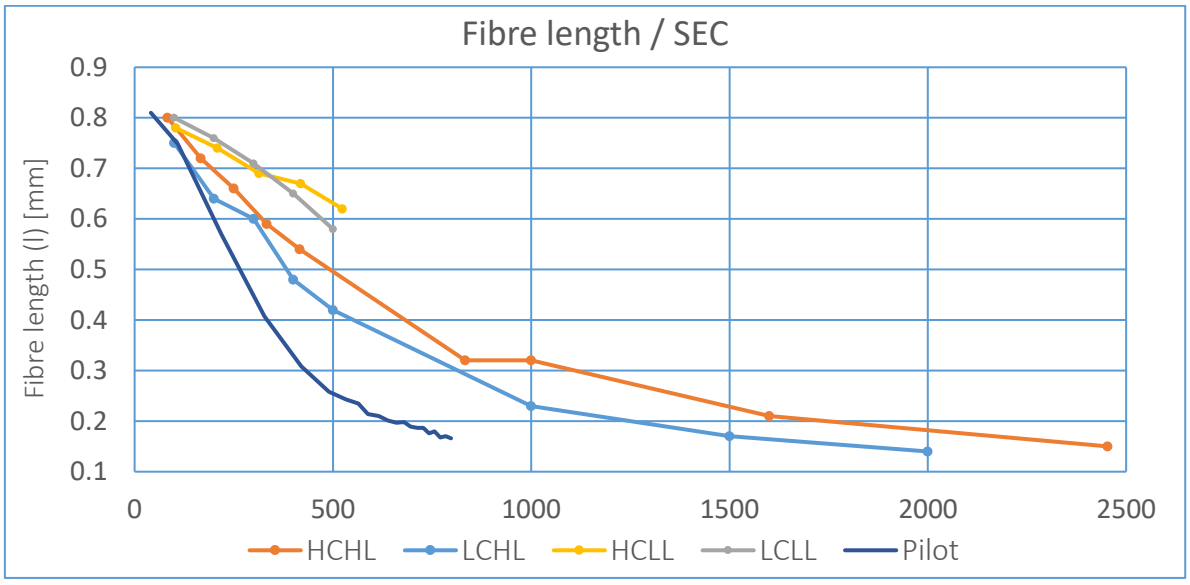
KOEAJOT								
Aika	**Aika (kum.)**	**Pvm**	**Missä**	**Kuka**	**Koeajon tarkoitus**	**Muuttujat**	**Ajot**	**Kommentit**
1.5 pv	1.5 pv	12/03	Åbo	E&V	1. Uuden erän sisäänajo	Teho	Teho 1 Teho 2 (Hiekoitus)	Kokeillaan uutta erää eri teholla/paljonko saadaan tehoja irti, kuinka pitkälle voidaan ajaa ilman terille menoa, mahdollinen hiekoitusajo. Huom! Näistä ajoista voisi lähettää 1-2 näytettä Kajaaniin, varmistetaan Ismolta onko tälle tarvetta/onnistuuko.
	1.5 pv							
	1.5 pv							
1.0 pv	2.5 pv	13/03	Åbo	E&V	2. Virtausnopeus	Virtausnopeus	30 l/min 60 l/min	Kokeillaan virtausnopeuden vaikutusta tehoon, massan ominaisuuksiin sekä ajettavuuteen/näytteenottoon, valitaan teho sisäänajon perusteella (oletus noin 5 kW/h), sakeus 3 %
	2.5 pv							
2.0 pv	4.5 pv	15/03	Åbo	E&V	3. Maksimisakeuden selvitys	Sakeus	6 % (5 %) (4 %)	Kokeillaan ajaa 6 % sakeudella, lasketaan tarvittaessa alemmas, verrataan edellisiin 3 % ajoihin SEC:in ja massan ominaisuuksien kannalta, virtausnopeus edellisten ajojen perusteella (oletuksena 30 l/min)
	4.5 pv							
	4.5 pv							
1.0 pv	5.5 pv	16/04			4. Päätepiste jauhatuksella tällä laitteistolla	Sakeus	5 % (todellinen oli 6,1%)	Ajetaan niin pitkälle kuin järkevästi päästään, isolla kuormituksella, näytteet 100 SEC välein SEC500 asti tehon vaikutuksen selvittämiseksi. Otetaan 3 litraa SEC500, SEC1000, SEC1500, SEC2000 jne riippuen kuinka pitkälle päästään. Viedään näistä lupaavimmat näytteet Kajaaniin.
	5.5 pv							
	5.5 pv							
1.0 pv	6.5 pv	17/04			4. " -	Sakeus	3,5 %	- " -
1.0 pv	7.5 pv	23/04			5. Tehon vaikutus (alussa)	Teho	5 % (mitattiin 5,8%, todellinen oli 5,5%)	Ajetaan SEC500 asti tasaisella 2,4 kW (5,1-2,66) kuormituksella, näytteet 100 SEC välein, lopputuotetta talteen paljon. Viedään näistä lupaavimmat näytteet Kajaaniin.
	7.5 pv							
1.0 pv	8.5 pv	25/04			5. - " -	Teho	3,5 %	- " -
KARAKTERISOINTI								
Aika	**Aika (kum.)**	**Pvm**	**Missä**	**Kuka**	**Mitä testataan**	**Menetelmät**	**Testien määrä**	**Kommentit**
3.0 pv	11.5 pv	4.-8.5.	Åbo	E&V	Lujuus	Labra-arkit (valmiina), tensile	15 arkkia (10-20 näytettä/arkki)	5 wt% MFC:tä per arkki, drainage-ajan mukaan voidaan nostaa tai laskea tätä. Testeihin tarvitaan 10-20 15mm liuskaa, yhdestä arkista saa 10-15 kpl eli 3 arkkia per näyte riittää hyvin. Mukana myös referenssinäyte ilman MFC:tä. SEC1500 myös 2.5%, 7.5% ja 10%.
1.0 pv	12.5 pv	4.5.	Aalto	V	Optiset, density, SEM,	Filmit	4 näytteestä 4	Parhaista näytteistä filmit, optiset testit ja tensile testit. Yhdet filmit säästetään SEM:iä varten.
3.0 pv	15.5 pv	7.-9.5.	Aalto	V	SEM-kuvat	Pakastekuivaus,	2-3 näytettä	
2.0 pv	17.5 pv		Aalto	E&V	Lujuus, MFC vs.	Labra-arkit, tensile	6 testiä (10-20	SEC1500 verrataan eri pitoisuuksina (2.5%-10%) kationiseen tärkkelykseen (pitoisuudet 2.5%-7.5%)
1.0 pv	18.5 pv		Åbo/Aalto	E&V	Repäisylujuus	Labra-arkit, tear	n. 5 testiä (10-20	Repäisylujuustestit valituille näytteille ylimääräisistä arkeista.
2.0 pv	20.5 pv		Aalto	V	Z-strength TMP:n lisäaineena	Labra-arkit, tensile	3-4 testiä (10-20 näytettä/testi)	Paras massa kahtena eri pitoisuutena, paras CS pitoisuus (ja paras CS + MFC yhdistelmä jos parempi kuin jompi kumpi pelkästään) TMP:n lisäaineena
1.0 pv	21.5 pv	-	Åbo	E&V	Kuitujen ominaisuudet	Valomikroskopia	muutamia	Valituista näytteistä kuva valomikroskoopilla, muun ehtimisen mukaan.
1.0 pv	22.5 pv	-	Åbo/Aalto	E&V	Vedensitomiskyky	WRV	muutamia	Valituista näytteistä WRV, muun ehtimisen mukaan.
1.0 pv	23.5 pv	Touko	Kajaani	E&V	Kuitujen ominaisuudet	FibreLab	max 10	Max 10 lupaavinta näytettä (ajoista 4, 1-6) mukaan Kajaaniin, voidaan myös jättää turhalta vaikuttava näytteitä pois.

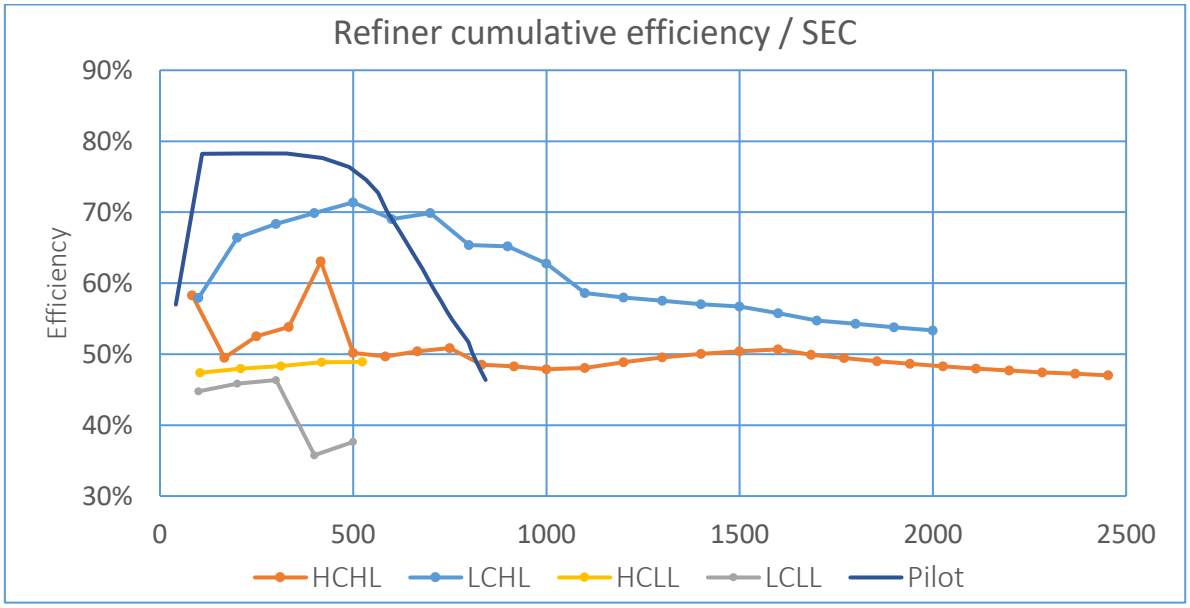
Appendix D – Additional charts






Schopper-Riegler / SEC
Schopper-Riegler
100
90
80
70
60
50
40
0
500
1000
1500
2000
2500
HCHL
LCHL
HCLL
LCLL
Pilot


Fibre length / SEC
Fibre length (l) [mm]
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
500
1000
1500
2000
2500
HCHL
LCHL
HCLL
LCLL
Pilot


Refiner cumulative efficiency / SEC
Efficiency
90%
80%
70%
60%
50%
40%
30%
0
500
1000
1500
2000
2500
HCHL
LCHL
HCLL
LCLL
Pilot